



# Evaluating Raman spectra of carbonaceous matter by automated, iterative curve-fitting



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## ABSTRACT

Raman spectroscopy of carbonaceous material (RSCM) estimates the maximum metamorphic temperature of coal, graphite and CM enclosed in metapelites. However, the evaluation of CM Raman spectra is often biased by subjectivity, which reduces the overall comparability of RSCM results. To decrease subjectivity, an automated evaluation software is presented. It is based on the iterative and simultaneous modeling of signal and baseline functions. Two new RSCM parameters are introduced, termed Raman Area Ratio (RAR) and Scaled Total Area (STA). These parameters are tested on a sample suite of organic rich shales and slates of the Teuschnitz Syncline (Thuringia, Germany) of well constrained very low to low metamorphic grade, defined by illite crystallinity and vitrinite reflectance. A correlation of both RSCM parameters with vitrinite reflectance verifies that the RSCM parameters reflect the metamorphic conditions. This correlation prevails at different excitation wavelengths (488 nm, 633 nm, 785 nm) used for the Raman measurements.

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## 1. Introduction

Raman spectroscopy is a widespread analytic method in geosciences. It is, for instance, used for mineral identification (Bartholomew, 2013; Bishop et al., 2004; Das and Hendry, 2011; Groppo et al., 2006; Haskin et al., 1997; Hope et al., 2001; Jehlička et al., 2009; White, 2009) analysis of fluid inclusions (Burke, 2001; Frezzotti et al., 2012; Guillaume et al., 2003; Pasteris et al., 1988; Rosso and Bodnar, 1995; Rosasco and Roedder, 1979; Van den Kerkhof and Olsen, 1990), analysis of phase transitions in relation to pressure and temperature (Auzende et al., 2004; Daniel et al., 1995; Gillet, 1996; Gunasekaran and Anbalagan, 2007; Lin, 2003; Palmer et al., 1994; Salje et al., 1993), to estimate coal rank (Hinrichs et al., 2014), examination and characterization of coal macerals (Guedes et al., 2010, 2012; Morga, 2011) and coke (Morga et al., 2015; Rantitsch et al., 2014) or to derive the maximum metamorphic temperature (Aoya et al., 2010; Beyssac et al., 2002b; Kouketsu et al., 2014; Lahfid et al., 2010). If Raman bands are characterized, spectral curve-fitting is often applied. However, the process of curve-fitting is commonly biased by subjectivity, because many programs require manual intervention, especially when baseline manipulation is required (Lünsdorf et al., 2014). Here, the 'Iterative Fitting of Raman Spectra' (IFORS) software is presented, which arose out of the necessity to evaluate Raman spectra multiple times without user guidance and was

initially designed for studies concerning geothermometric information obtained by RSCM.

RSCM is based on the transformation of CM to graphite. The structural reorganization in relation to the degree of metamorphism can be analyzed by Raman spectroscopy (Wopenka and Pasteris, 1993; Yui et al., 1996; Beyssac et al., 2002a; Lahfid et al., 2010; Aoya et al., 2010; Beyssac and Lazzeri, 2012; Kouketsu et al., 2014). In the case of metasedimentary rocks, Beyssac et al. (2002b) showed that the CM transformation depends mainly on the metamorphic temperature and that the structural state of the CM is not influenced by retrograde processes. Thus, the maximum metamorphic temperature can be derived by RSCM. This is achieved by describing the Raman spectrum by a user defined series of functions (Gauss, Lorentz, Voigt, etc.) and by forming a function parameter ratio that is linked to the metamorphic temperature. The average function parameter ratio of a given sample is influenced by several biasing factors that can be sorted in three groups, i.e. bias due to the CM (heterogeneity, anisotropy, etc.), bias due to the Raman system (e.g. laser wavelength) and bias due to curve-fitting strategy (Lünsdorf et al., 2014). Bias due to the curve-fitting strategy is induced by the operator himself, who introduces subjectivity by manual intervention and thereby reduces the general comparability of RSCM results (Lünsdorf et al., 2014). To overcome the operator induced subjectivity, Lünsdorf et al. (2014) concluded that an automated curve-fitting routine is needed.

Here we present an iterative algorithm that is based on the randomized mutation of function parameters. The approach follows the idea that the recorded spectrum consists of high-frequency signal components

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and low-frequency baseline components with added normal distributed noise (Schulze et al., 2005). The signal components are described by pseudo-Voigt (PV) functions and the baseline component by a polynomial, which are modeled simultaneously.

The main purpose of the algorithm is the batch fitting of CM spectra. To test if the IFORS software is able to describe the transformation of CM, a sample set of very low grade metamorphic conditions has been collected. These conditions are defined through illite crystallinity and vitrinite reflectance data after Kunert (1999); see Table 1 for details. Very low grade metamorphism is used here in the sense of Frey (1987). It describes the pressure and temperature conditions after early diagenesis to the onset of greenschist facies, which covers a temperature field of approximately 100 to 300 °C. This metamorphic range is, on the basis of illite crystallinity (IC), subdivided in the diagenetic zone, anchizone and epizone (Frey, 1987; Kisch, 1990). In IC the full width at half maximum (FWHM) of the diffractometric basal X-ray reflection of illite is measured and the zone boundaries are 0.42 between the diagenetic zone and anchizone and 0.25 for the transition from the anchizone in the epizone (Kisch, 1990; Kisch et al., 2004).

Because IFORS generates results with variable numbers of PV functions, two new Raman parameters are introduced that are independent of the number of functions. The Raman Area Ratio (RAR) uses a ratio of PV function area parameters and the Scaled Total Area (STA) method utilizes the Scaled Total Area of all PV functions of the curve-fitted spectrum. Both parameters describe the transformation of CM during very low grade metamorphism.

## 2. Approach & algorithm

During evaluation of Raman or other spectral data the baseline is often estimated by a linear, a polynomial or a spline function (Baek et al., 2011; Bradley, 2007; Cao et al., 2007; de Rooi and Eilers, 2012; Rowlands and Elliott, 2011) and these function's values are usually subtracted from the spectrum before the signal functions are modeled (Bradley, 2007). This approach requires the discrimination of baseline and signal data points. However, it is often difficult to separate baseline data points from signal data points, especially when many Raman bands

are overlapping. In addition, linear functions are often not able to describe the inherent curvature of the baseline and polynomials need to be constrained properly to avoid fluctuation of the polynomial, which is especially important at the endpoints of the spectrum and when high degree (>6) polynomials are used.

In our approach the signal and baseline components of the spectrum are modeled iteratively at the same time. The theoretical intensity of a Raman band is described by a Lorentz function (Rull, 2012). However, impurities and structural defects in the sample and the instrument profile function add a normally distributed component to the Lorentzian shape of a Raman band (Vácz, 2014). Therefore, the pseudo-Voigt (PV) profile (Eq. (1)) given in Sanchez-Bajo and Cumbre (1997) is chosen, because it is a linear combination of the Gauss and Lorentz profile and describes the shape of the recorded Raman bands more appropriately.

$$pV = I_0 \cdot \left( \eta \frac{1}{1 + \frac{(x-x_0)^2}{w^2}} + (1 - \eta) \cdot \exp\left(-\ln(2) \frac{(x-x_0)^2}{w^2}\right) \right) \quad (1)$$

Where  $I_0$  is the height,  $x_0$  the central position,  $\eta$  the shape factor which controls the fractions of the Lorentz and Gauss components and  $2w$  is the FWHM of the PV function.

### 2.1. Preprocessing

A Raman spectrum represents the accumulation of dispersed light over the fixed distance of the detector width, i.e. usually  $1024 \times 256$  equidistant pixels. As the dispersion depends on the wavelength, the data point distance decreases from short wavelengths to longer wavelengths (Fig. 1a). Therefore, the data point distance needs to be equalized. This is done by generating a new x-axis with the same number of data points as the original spectrum equally distributed from the lowest wavenumber to the highest wavenumber (Fig. 1b). The intensity values at the generated wavenumbers are derived by linear interpolation from the original data (Fig. 1c).

**Table 1**  
The sample locations with according illite crystallinity and vitrinite reflectance values. (\*) indicates that the  $R_r$  value is calculated as  $(2R_{\max} + R_{\min})/3$  (Taylor, 1998). std = standard deviation,  $R_r$  = random reflectance, n = number.

Sample code		Coordinates		Illite crystallinity		Vitrinite reflectance [%]		
Kunert (1999)	This study	Lat (N)	Long (E)	$\Delta^{\circ}2\theta$	std	$R_r$	std	n
FR129	KL2-11	50°15'47.66"	11°31'18.53"	0.318	0.013	(*)4.62	0.21	40
FR105	KL2-12	50°17'19.22"	11°33'29.31"	0.354	0.016	(*)4.43	0.28	40
	KL2-13C	50°17'50.38"	11°35'21.64"			(*)4.31	0.30	40
FR109	KL2-17	50°21'17.61"	11°30'39.25"	0.292	0.000	(*)4.58	0.27	40
FR128	KL2-18	50°19'36.3"	11°22'39.61"	0.392	0.007	2.28	0.19	40
FR126	KL2-19	50°18'22.67"	11°21'23.60"	0.349	0.013	2.48	0.29	40
FR125	KL2-20	50°19'34.81"	11°21'7.6"	0.344	0.003	1.73	0.18	50
FR118	KL2-21	50°19'35.30"	11°22'36.18"	0.213	0.005	(*)5.61	0.23	36
FR117	KL2-22	50°28'48.51"	11°23'34.44"	0.192	0.007	(*)6.37	0.44	40
FR122	KL2-3	50°24'3.23"	11°21'10.49"	0.386	0.012	3.14	0.28	40
FR127	KL2-4	50°21'43.33"	11°24'20.45"	0.341	0.014	3.90	0.33	30
FR112	KL2-5	50°23'42.67"	11°29'23.64"	0.235	0.008	(*)4.89	0.27	40
FR111	KL2-7	50°22'20.8"	11°31'4.37"	0.237	0.004	(*)4.77	0.32	40
FR111	KL2-8	50°22'13.22"	11°31'10.41"	0.237	0.004	(*)5.14	0.32	40
FR142	KL5-12	50°17'12.3"	11°21'44.86"	0.301	0.008	(*)3.71	0.22	40
FR141	KL5-13	50°18'49.21"	11°23'42.44"	0.367	0.000	2.87	0.19	40
FR139	KL5-14	50°20'3.90"	11°24'39.33"	0.306	0.003	2.44	0.21	40
	KL5-4	50°23'15.80"	11°18'51.77"			2.43	0.25	40
FR185	KL5-5	50°24'2.0"	11°18'49.49"	0.374	0.004	(*)3.22	0.17	40
	KL5-6	50°23'49.17"	11°18'53.67"			2.21	0.24	40
FR195	KL5-10A	50°20'43.93"	11°18'0.35"	0.516	0.005	2.08	0.18	40
FR193	KL5-7	50°23'8.76"	11°19'12.2"	0.449	0.011	2.52	0.24	26
FR197	KL5-11	50°18'31.38"	11°19'14.92"	0.433	0.018	2.23	0.16	30

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