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THERMOVAPORISATION: A SCREENING TOOL FOR THE GAS-SORPTIVE PROPERTIES OF SOURCE ROCKS

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Abstract

Here we report the development of a new geochemical logging method to evaluate the amount and composition of sorbed gas within source rocks quickly and inexpensively, thereby providing a practical tool for the rapid identification of “sweet spots” or heterogeneities within vertical profiles. Thermovaporisation GC-FID (Tvap) forms the basis of the screening method and can be easily run alongside Rock-Eval pyrolysis in high resolution. A fairly good correlation of S2 normalised Tvap gas yields with the rocks TOC normalised measured Langmuir amounts (n_L) assessed using standard petrophysical methods (e.g. excess sorbed methane versus pressure curves) demonstrates that Tvap is capable of defining the basic sorption characteristics of source rocks or gas shales. The Tvap screening tool excels at detecting zones (organofacies/lithofacies) and related heterogeneities in the sorption behaviour of the respective rocks, but not in directly detecting sorption properties. Nevertheless, adsorptive property profiling is possible for large data sets by including direct integration of Langmuir parameters.

1. Introduction

Quantifying the gas stored in shale-gas reservoirs in “free” and “sorbed” states is critical for the assessment of Gas-In-Place (GIP) and the design of effective production strategies. “Free”, hence easy-to-produce gas is found in the rocks pore volume and fractures; sorbed gas is found adsorbed on the surfaces of

organic matter or clay minerals, but also absorbed in organic polymer structures or dissolved in bitumen or pore fluids (Ross and Bustin, 2009; Gasparik et al., 2014). The sorption capacity as an important fraction of the total gas storage capacity is usually assessed by deploying rather slow and costly petrophysical methods for a small number of “representative” samples and a limited range of experimental conditions and gas species.

Here we describe how T_{vap} can be effectively used as a screening tool to evaluate the amount of sorbed gas within source rocks quickly and inexpensively. The T_{vap} tool works on the principle that small amounts of C₁₋₅ gases in powdered rock samples can be released by temperature triggered desorption at 300 °C from organic and mineral matter surfaces. We illustrate its applicability for assessing gas sorptive properties using results of experiments conducted on immature to mature samples of Cambrian Alum Shale (Denmark, Sweden), Jurassic Posidonia Shale (Germany), and the Late Mississippian Barnett Shale (Fort Worth Basin, Texas) that were studied within the GASH- project (Gas Shales in Europe). T_{vap} gas yields and directly measured sorption capacity, the Langmuir amount (n_L), were correlated (Table 1; Figure 1) and data from the Barnett Shale Mesquite-1 well illustrates how the T_{vap} gas yields can be used for rapid adsorptive property profiling (Fig. 2).

2. Experimental

Langmuir amounts (n_L) expressing the maximum methane sorption capacity at infinite pressure were determined on dried powder at 65 °C; detailed procedures and results are described in Gasparik et al. (2014) along with total organic carbon (TOC) concentrations. Rock-Eval was performed using a Rock-Eval 6 instrument. T_{vap} and open-system pyrolysis was performed using a

Quantum MSSV-2 Thermal Analyzer© interfaced with an Agilent GC 6890A gas chromatograph as described in Han et al. (2015).

3. Results and discussion

Plotting calculated Langmuir amounts n_L (Fig. 1a) and T_{vap} C₁₋₅ gas yields (Fig. 1b) of all Posidonia, Barnett, and Alum Shale samples versus TOC content a more or less linear relationship between the two parameters can be expected, because TOC is known to positively correlate with the adsorption capacity of source rocks (Ross and Bustin, 2009). Nevertheless, this correlation is not exact and the goodness of fit varies between formations because other factors such as clay content, maturity, and kerogen type also play important roles in determining the overall sorption capacity (Ross and Bustin, 2009; Zhang et al., 2012; Gasparik et al., 2014). T_{vap} gas yields of immature Posidonia, Barnett, and Alum Shale samples (squares in Fig.1b) are generally higher than those of the more mature equivalents (crosses and circles in Fig. 1b), which also finds its expression in a very good correlation between T_{vap} gas yields and Rock-Eval S2 values (Fig. 1c). The amount of sorbed gas decreases with increasing maturity in the course of petroleum generation (loss of S2) indirectly confirming results of Han et al. (2015) and Ziegls et al. (2017), who reported that retention of petroleum (S1) takes mainly place on the Rock-Eval S2 portion of organic matter. Interestingly, T_{vap} gas yields fall along different gradients for samples from the three different shales. i.e., gas yields for the Posidonia Shales are appreciably lower than those for Alum Shales with near equivalent S2 (Fig. 1c). To better characterise this kerogen specific sorption behaviour T_{vap} gas yields are normalised to S2 (Table 1). Plotted against Hydrogen Index (HI; Fig. 1d) S2 normalised T_{vap} gas yields are still higher for immature Alum Shale samples

than for immature Barnett and Posidonia Shale samples (squares in Fig. 1d) providing evidence that the chemical structure of kerogen itself influences its gas sorptive properties. It seems that aromaticity primarily controls sorption capacity because a very good correlation can be obtained from plotting S2 normalised T_{vap} gas yields versus an open-system pyrolysis derived ratio of *o*-xylene/nonene which represents the aromaticity of kerogen (Fig. 1e). Focusing only on immature samples (squares), the Alum Shales exhibit highest aromaticity levels, most likely caused by uranium irradiation (Yang et al., 2018), followed by Barnett Shales and lowest for the Posidonia Shales. This directly confirms results of Zhang et al. (2012), who reported that sorption capacity decreases in the order Type III Cameo Coal, Type II Woodford Kerogen, Type I Green River Kerogen, and Ziegler et al. (2017), who showed for Mandal Fm. source rocks that gas retention is positively correlated to kerogen aromaticity. That aromaticity of residual organic matter increases during maturation due to the loss of oil precursor structures is also evident from Fig. 1e and provides the best explanation for increased S2 normalised T_{vap} gas yields for all mature samples (circles Fig. 1d). This is in line with results of Ross and Bustin (2009) who showed that gas sorption capacity increases with maturation for Jurassic and Devonian-Mississippian Shales, especially within the gas window and is most likely related to the development of organic porosity. The subtle decrease in sorption capacity as expressed in S2 normalised T_{vap} gas yields observed for samples within the oil window (crosses in Fig. 1d) can be explained by the presence of bitumen occupying gas sorptive sites. Thus, a good although not perfect, positive correlation of S2 normalised T_{vap} gas yields versus TOC normalised n_L values exists (Fig. 1f) demonstrating that qualitatively meaningful information

concerning sorption capacity can be extracted from the T_{vap} approach. TOC normalised n_L values and S₂ normalised T_{vap} gas yields versus vitrinite reflection plots (Fig. 1g and h, respectively) illustrate that similar sorption capacity distributions are observed across all gas shale sample. For Posidonia Shales, sorption capacity increases with maturity, but slightly lower sorption capacities occur in the main oil window. TOC normalised n_L values and S₂ normalised T_{vap} gas yields of the immature Alum and Barnett Shale rocks are higher than the most mature Posidonia shales from the HAD well presumably due to their higher aromaticity.

The advantage of T_{vap} gas yields as a proxy for a rocks gas sorption capacity is that it can be used as a screening tool for rapid sorptive property profiling in heterogeneous shale successions, here exemplified for the Barnett Shale Mesquite-1 well (Fig 2). From the Barnett Top on downwards, S₂ normalised T_{vap} gas yields are centred on a line at ~0.4 mg/g S₂ which expresses the average of all samples from the well. Deviation of samples from this line indicates a change in sorption capacity either due to a change in organic matter type or mineralogical factors. Positive outliers with values up to 0.8 mg/g S₂ are encountered when clay contents are highest, i.e., above 50%, which can be deduced from values lower than 0.5 in the “brittle minerals ratio” log (data from Han et al. (2015)). High clay contents can lead to higher sorption capacities as discussed in various papers (e.g. Ross and Bustin, 2009; Gasparik et al., 2012). Relatively high S₂ normalised T_{vap} gas yields of ~1 in the Marble Falls Fm. can be attributed to a completely different, carbonate dominated lithofacies which is characterised by very low S₂ values.

4. Summary and Outlook

Screening measurements cannot replace established procedures for determining correct and reproducible adsorption isotherms; however, the T_{vap} gas yields tool is capable of quickly differentiating the sorption behaviour related to mineralogy and/or organic matter type within heterogeneous shale sequences. The technique offers a better sample selection for classic petrophysical measurements that would cover the possible range of sorption capacities found in a well, and thereby provides the opportunity to extrapolate lab determined Langmuir parameters for distinct lithofacies over extended vertical profiles.

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Table 1

Geologic background information, Total organic carbon (TOC), Vitrinite Reflectance (R_o), Rock-Eval S2 and HI, gas sorption data acquired using petrophysical methods and T_{vap} GC-FID, and kerogen aromaticity assessed using open-system pyrolysis GC-FID for all studied shale samples.

Figure 1: Assessing sorption capacity

a) Langmuir amounts n_L and b) T_{vap} gas yields versus the shales organic matter richness defined by TOC. c) T_{vap} gas yields versus the amount of labile kerogen defined by Rock-Eval S2. S2 normalised T_{vap} gas yields versus d) Rock-Eval HI, e) kerogen aromaticity defined by the ratio *o*-xylene/*n*-C_{9:1} measured using open-system pyrolysis, and f) TOC normalised n_L . g) TOC normalised n_L and h) S2 normalised T_{vap} gas yields versus maturity defined by vitrinite reflection.

Figure 2: Adsorptive property profiling

Adsorptive rock properties as defined by S2 normalised T_{vap} gas yields can be easily compared in geochemical depth profiles to standard Rock-Eval screening data (e.g. TOC or S2) or mineralogical information (e.g. brittle minerals ratio which is the sum of all minerals (quartz + feldspars + total clays + total carbonates) minus total clays over the sum of all minerals). Mesquite-1 well data from Han et al. (2015).

Table 1

Ref.#	Background		Maturity	TOC	Rock Eval	Petrophysical		Tvap		OpenPy	
	Shale Formation	core/ outcrop*				Methane Sorption data		Gas Sorption data			Aromaticity
						n_L	n_L	C_{1-5}	C_{1-5}		
			VRr		S2	n_L	n_L	C_{1-5}	C_{1-5}	o -xylene/ n -C _{9:1}	
			(%)	(wt.%)	(mg/g rock)	(mmol/g rock)	(mmol/g TOC)	(mg/g rock)	(mg/g S2)*100	(kg/kg)	
1	Posidonia	Wickensen	0.5	14.14	66.64	0.302	2.14	0.081	0.122	0.66	
2	Posidonia	Wickensen	0.5	11.68	60.56	0.235	2.01	0.065	0.107	0.51	
3	Posidonia	Wickensen	0.5	11.66	65.44	0.186	1.59	0.059	0.091	0.77	
4	Posidonia	Harderode	0.9	9.30	30.17	0.140	1.50	0.021	0.070	0.44	
5	Posidonia	Harderode	0.9	6.78	21.20	0.147	2.17	0.038	0.177	0.42	
6	Posidonia	Harderode	0.9	10.90	33.47	0.106	0.97	0.023	0.068	0.35	
7	Posidonia	Haddessen	1.5	6.72	4.90	0.175	2.60	0.019	0.378	0.76	
8	Posidonia	Haddessen	1.5	7.72	3.74	0.163	2.11	0.011	0.287	0.93	
9	Posidonia	Haddessen	1.5	7.68	5.11	0.163	2.13	0.009	0.181	0.69	
10	Posidonia	Haddessen	1.5	10.49	5.97	0.213	2.03	0.011	0.187	0.80	
11	Alum	Hällekis-1	0.5	14.01	60.88			0.245	0.402	3.57	
12	Alum	Hällekis-1	0.5	13.38	64.12			0.248	0.387	3.04	
13	Alum	Hällekis-1	0.5	11.14	59.79			0.338	0.565	1.51	
14	Alum	Hällekis-1	0.5	11.06	56.56			0.279	0.494	1.52	
15	Alum	Hällekis-1	0.5	10.21	55.02			0.255	0.464	1.23	
16	Alum	Djupvik*	0.5	8.14	35.70	0.204	2.51	0.108	0.302	0.88	
17	Alum	Ottenby*	0.9	7.25	28.76	0.191	2.63	0.049	0.169	0.44	
18	Alum	Gislövshammar*	2.0	2.36	0.72	0.095	4.03	0.025	3.431	4.36	
19	Alum	Skelbro	2.3	5.67	0.56	0.201	3.54	0.005	0.963	15.43	
20	Alum	Skelbro	2.3	7.07	0.70	0.223	3.16	0.017	2.431	970.68	
21	Alum	Skelbro	2.3	7.73	0.92	0.232	3.00	0.022	2.430	10.80	
22	Alum	Skelbro	2.3	5.22	0.47	0.162	3.10	0.003	0.667	11.49	
23	Alum	Skelbro	2.3	4.38	0.54	0.182	4.16	0.005	0.850	12.09	
24	Barnett	San Saba*	0.5	11.70	57.90	0.311	2.66	0.140	0.241	0.84	
25	Barnett	Ron Cheek	0.9	5.59	15.73	0.108	1.92	0.036	0.228	0.44	
26	Barnett	Mesquite-1	1.0	1.13	1.69	0.042	3.70	0.016	0.961		
27	Barnett	Mesquite-1	1.0	0.39	1.04	0.019	4.83	0.037	3.562	0.88	
28	Barnett	Mesquite-1	1.0	4.53	11.59	0.114	2.53	0.068	0.586	1.65	
29	Barnett	Mesquite-1	1.0	2.71	3.45	0.094	3.48	0.017	0.484		
30	Barnett	Mesquite-1	1.0	3.77	9.82	0.100	2.64	0.042	0.425		
31	Barnett	Mesquite-1	1.0	7.98	14.54	0.226	2.84	0.096	0.658	1.23	
32	Barnett	Mesquite-1	1.0	6.57	11.39	0.157	2.39	0.041	0.361	0.93	
33	Barnett	Mesquite-1	1.0	2.60	7.21	0.083	3.19	0.025	0.350		
34	Barnett	Mesquite-1	1.0	4.27	8.78	0.116	2.72	0.026	0.295		
35	Barnett	Mesquite-1	1.0	4.92	10.22	0.161	3.26	0.022	0.219	0.71	
36	Barnett	Mesquite-1	1.0	2.76	5.02	0.040	1.46	0.013	0.259		

Data for **VRr** = Vitritine reflectance, **TOC** = total organic carbon, and **n_L** = Langmuir amount defining the maximum methane sorption capacity at infinite pressure are taken from Gasparik et al. (2013).

S2 = amount of hydrocarbons generated during Rock Eval pyrolysis between 300 and 650°C (mg/g rock)

Figure 1

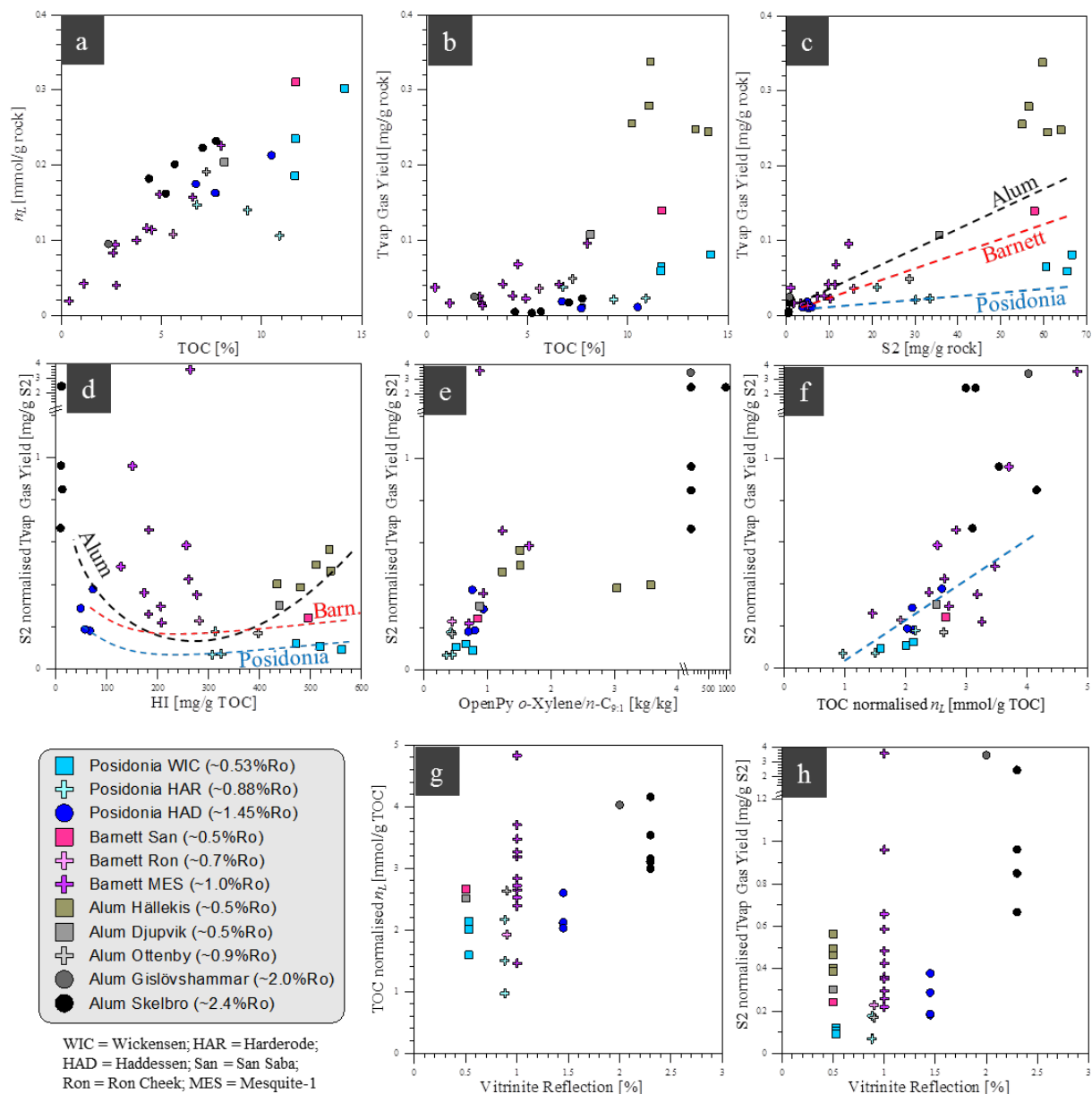


Figure 2

