



Determination of maximal amount of minor gases adsorbed in a shale sample by headspace gas chromatography



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ABSTRACT

In this paper, we present a novel method for determining the maximal amount of ethane, a minor gas species, adsorbed in a shale sample. The method is based on the time-dependent release of ethane from shale samples measured by headspace gas chromatography (HS-GC). The study includes a mathematical model for fitting the experimental data, calculating the maximal amount gas adsorbed, and predicting results at other temperatures. The method is a more efficient alternative to the isothermal adsorption method that is in widespread use today.

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1. Introduction

Because of the great demand for energy resources in the world, shale gas (mainly in the form of methane) trapped inside shale formations deep underground [1] is becoming an increasingly important alternative source of natural gas, especially in North America [2]. However, the current development of this resource in China has been limited, even though it is estimated that the country has the world's largest shale gas reserves in the world [3]. In addition to the difficulties in the existing production techniques and the geological conditions in China, the lack of proven technologies that can identify the deposits of interest (i.e., the enriched zones) in a timely manner is also a major problem. Therefore, methods for effectively and efficiently evaluating the presence and amount of shale gas in a particular location are of great interest.

Gas species in deep shale formations are present in two forms; i.e., free gas and adsorbed gas [4]. The amount of free gas in a shale sample can be determined based on sampling and geological information; e.g., the degree of gas saturation and porosity [5]. The amount of adsorbed gas is typically determined using a Langmuir isothermal adsorption approach [6,7], in which the isothermal equilibrium adsorption capacity is measured at different pressures, from which the Langmuir constants (i.e., the adsorption constant

and maximal adsorption capacity) are obtained. However, this approach is very time-consuming, usually requiring more than 12 h to get one data point in the test [8].

Although methane is the dominant component in gas recovered from shale formations, there are some minor species (e.g., ethane and CO₂) present in shale samples, as well. The amount of these minor gases can be significant and thereby reduce the amount of methane adsorbed in the shale sample due to competitive adsorption [9]. As a result, the isotherm adsorption test can overestimate the amount of methane in the sample and a correction must be applied to account for the presence of these other gases. Previous studies [9] have already taken these multiple components into account, and an equation for calculating the total adsorbed gas (i.e., the sum of all components) has been derived. i.e.

$$G_a = \sum_{i=1}^n G_{aL,i} \frac{y_i p}{p_{L,i} \left(1 + \sum_{j=1}^n y_j \frac{p}{p_{L,j}} \right)} \quad (1)$$

where G_a and G_{aL} represent the amount of adsorbed gas and the maximal amount of adsorbed gas, respectively. p and p_L represent the formation pressure and Langmuir pressure, respectively. y represents the volume fraction of the interest gas species.

However, this equation requires the adsorption constant and the maximal adsorption value for each of the gases present in the sample. The isothermal adsorption method calls for an isothermal measurement for each of the pure gas species present in the sample; i.e., a major data collection effort. Therefore, an alternative

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method that can efficiently determine the Langmuir constants is highly desirable.

According to Langmuir adsorption kinetics, the maximal amount of adsorbed gas species (which reflects the maximal void sites) is a key parameter that affects the gas adsorption rate. This model is widely used in building construction studies and environmental investigations that explore the sorption and desorption behavior of volatile species [10,11]. In most cases (e.g., the release of formaldehyde from building materials [12,13]), custom-designed chambers are used to measure the gas sample in the headspace of the chamber. This customized approach raises questions about reproducibility, standardization, and comparability of the reported results.

In contrast, headspace gas chromatography (HS-GC) is a proven tool for quantifying volatile species in both liquid samples with complicated matrices and solid samples [14,15]. Recently, we have developed a new static (equilibrium) HS-GC method for the determination of adsorption partition coefficient (K_d) of ethane in a shale sample using a commercial HS-GC system [15].

In this paper, we report on a novel method, based on the time-dependent release of gaseous species from shale samples and their measurement by HS-GC that is suitable for use in the determination of the maximum adsorption capacity (N) of the gas species contained in the samples. Ethane, a minor gas species typically found in shale samples, is used to demonstrate the method.

2. Materials and methods

2.1. Samples

The shale sample was obtained from a shale gas reservoir located in Sichuan province, China. The sample (air-dried) was ground by an electromagnetic ore grinder and screened to 60–80 mesh (the average particle size is 214 μm) and stored in a silica gel dryer with a paper sampling bag for 24 h for further use. The specific surface area and density of the shale particles were 5.60 m^2/g and 2.59 g/cm^3 , respectively, which were determined by the standard techniques that are used for particle characterization [16]. The uncertainty in specific surface area and particle density determination are 10% and 0.01 g/cm^3 , respectively.

2.2. Apparatus and operations

An electromagnetic ore grinder (DF-3, Huanan Instrument, China) was used in the preparation of the powder samples. A GC system (Agilent 7890A, USA) with an automatic headspace sampler (DANI HS 86.50, Italy) was used for the HS-GC measurements. The GC system was equipped with a flame ionization detector and a DB-5 capillary column (Agilent, USA) operating at a temperature of 40 $^\circ\text{C}$ with nitrogen carrier gas (flow rate = 3 mL/min). The headspace operating conditions were as follows: strong shaking for sample equilibration at the temperature of interest; vial pressurization time = 0.2 min; and sample loop fill time = 0.2 min. The volume of the headspace sample vials was 21.6 mL. The volume of the sample loop was 3 mL.

3. Results and discussion

3.1. Principle of the method

It is widely accepted that the adsorbed gas in shale can be calculated by the Langmuir isothermal adsorption model where the adsorption take place on the outer surface and inner surface (open to outer circumstance) of shale samples, which is different from the cases in building and environmental field that the inner

transportation is considered [17]. Based on the assumptions of the model, the rates of adsorption and desorption can be expressed as

$$v_a = k_1(1 - \theta)pN \quad (1.1)$$

and

$$v_d = k_2\theta N \quad (1.2)$$

where v_a and v_d represent the rates of adsorption and desorption, respectively; N ($\mu\text{mol}/\text{g}$ sample) represents the maximal amount of adsorption; p (MPa) represents the pressure; and θ represents the fraction of the adsorption sites occupied, i.e., the actual amount of gas adsorption on the sample surface divided by the maximal amount of adsorption on the sample; k_1 and k_2 are the adsorption and desorption rate constants, respectively.

When adsorption/desorption equilibrium is reached, the adsorption rate equals to the desorption rate, i.e.

$$k_1(1 - \theta)pN = k_2\theta N \quad (2)$$

Eq. (2) can be rewritten as

$$\theta = \frac{bp}{1 + bp} \quad (3)$$

where $b = k_1/k_2$ is the adsorption constant.

Before the equilibrium state is reached, the net desorption rate equation at time t can be expressed as

$$\frac{dN_g}{dt} = k_2\theta N - k_1(1 - \theta)pN \quad (4)$$

where N_g ($\mu\text{mol}/\text{g}$ sample) is the amount of gas species in headspace at time t .

By definition θ , the actual fraction of the surface sites occupied, can be expressed as

$$\theta = \frac{N_0 - N_g}{N} \quad (5)$$

where N_0 ($\mu\text{mol}/\text{g}$ sample) is the initial amount of gas adsorbed on the sample surface.

From Eq. (4), Eq. (5) and the state equation of gas, i.e.

$$p = \frac{N_g RT}{V_g} \quad (6)$$

where V_g (mL), R (J \cdot μmol^{-1} K^{-1}) and T (K) are the void volume of gas phase, the molar gas constant and temperature, respectively, the rate of desorption is

$$\frac{dN_g}{dt} = \alpha N_g^2 + \beta N_g + \gamma \quad (7)$$

where

$$\alpha = -\frac{k_1 RT}{V_g} \quad (7.1)$$

$$\beta = -\frac{k_1 RT(N - N_0) + k_2 V_g}{V_g} \quad (7.2)$$

and

$$\gamma = k_2 N_0 \quad (7.3)$$

Since the amount of gas species in the gas phase (i.e., N_g) increases with increasing time during the desorption process, $dN_g/dt > 0$. From Eq. (7.1), $\alpha < 0$. Therefore, the quadratic function, Eq. (7), must have two points of intersection with the axis in the real number range. Hence, Eq. (7) can be rewritten as the two-point form of quadratic function, i.e.

$$\frac{dN_g}{dt} = \alpha(N_g - m)(N_g - n) \quad (8)$$

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