



A simple method for correcting for the presence of minor gases when determining the adsorbed methane content in shale



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HIGHLIGHTS

- Develop an approach to use the HS-GC determined parameters in gas calculation.
- Convert the adsorption equilibration partition coefficient to Langmuir constants.
- The Langmuir constants of minor gases used in gas calculation are from HS-GC test.

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ABSTRACT

This paper demonstrates a novel approach for correcting for the presence of minor gases when determining the adsorbed methane content in shale. Based on the widely used Langmuir isotherm in calculating the adsorbed gas, an equation is derived that converts the adsorption equilibrium partition coefficient (K_d) and maximal amount of adsorbed gas (N) at low pressure to Langmuir pressure (p_L). Headspace gas chromatography (HS-GC) is used to determine the K_d and N of the minor gas species present in the shale. The results indicate that the method satisfactorily accounts for the presence of minor gases when estimating the amount of adsorbed methane. This HS-GC method is much more efficient than the isothermal adsorption test currently used for the measurement of adsorption parameters of minor gas species in shale. Therefore, this new approach will improve the speed and accuracy of estimating the amount of adsorbed methane in shale deposits.

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1. Introduction

Natural gas production from hydrocarbon-rich shale formations, known as “shale gas”, is one of the most rapidly growing new sources of energy. For example, in recent years, there has been rapid progress in the development of unconventional shale gas recovery in North America [1]. To produce similar results in China, which also has abundant estimated reserves of shale gas [2], additional research is needed, including development of techniques for effectively and efficiently estimating the amount of shale gas in particular formations. This information is vital for identifying locations of interest (i.e., enriched zones) that would justify the investment of resources to commercialize shale gas production.

In addition to the free gas which dissociates with shale pores, the adsorbed gas can account for ~20–80% of the total gas

entrapped in underground shale gas reservoirs [3,4]. When only methane (the major component of shale gas) is taken into consideration, the typical Langmuir equation [5] can be used, i.e.,

$$G_a = \frac{G_{al}p}{p + p_L} \quad (1)$$

where two parameters (i.e., Langmuir volume (G_{al}) and Langmuir pressure (p_L) of adsorbed methane) are required. Although these parameters can be obtained by the isothermal adsorption test [6,7], the experimental procedure required is complicated and time-consuming. In most cases, the problem is further complicated by the presence of several minor gas species (e.g., ethane and carbon dioxide) that coexist in shale. The neglecting of these coexisting minor gases results in an over-estimation of the adsorbed methane in shale if the conventional Langmuir equation is used. In order to correct for the presence of minor gases, an extended Langmuir equation has been proposed to calculate the adsorbed methane gas (G_a^{Me}) in shale [8–10]; i.e.,

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$$G_a^{Me} = G_{al}^{Me} \frac{y_{Me} p}{p_L^{Me} \left(1 + \sum_{i=1}^n \frac{y_i p}{p_L^i} \right)} \quad (2)$$

This expression is similar to Eq. (1), except that in addition to the Langmuir constants (i.e., G_{al}^{Me} and p_L^{Me}) for methane, the Langmuir pressures for the minor gas (i.e., p_L^i) are also required. Although the amounts of these minor gas species adsorbed in shale are much lower than that of methane, the same procedures must be individually performed for each gas species in the isothermal adsorption test [11]. Therefore, a significant amount of time is required to evaluate the amounts of all of the adsorbed gases in the shale samples.

The isothermal adsorption test is designed to simulate the adsorption behavior of gases at various pressures. For methane, the isothermal adsorption test conducted at high pressure is necessary to obtain the Langmuir constants because of the high partial pressure of methane in most shale gas reservoirs [12]. For the minor gases, their partial pressures could be much lower than that of methane [12]. In that case, the adsorption behavior can be described by their partitioning coefficients between the vapor and solid phases when the linear sorption isotherm is valid, which can then be converted to parameters used in the Langmuir equation. This approach greatly reduces the time required to determine the amount of methane adsorbed in the shale.

There are several methods that can be used for the determination of partition coefficients in a solid–vapor adsorption system [13–16], however are usually based on custom-designed devices. Recently, we have developed two novel methods, based on the commercial headspace gas chromatographic system (HS-GC), for the determination of the adsorption equilibrium partition coefficient and maximal amount of adsorbed gas for the minor gases adsorbed in shale [17,18]. Thus, the method lends itself to relatively easy standardization procedures. Compared with the isothermal adsorption test, all these methods are much more efficient for the determination of the adsorption-related parameters for the minor gases adsorbed on shale. However, in the practical applications, the key step is the conversion of the parameters measured by these efficient methods to the parameters that appear in the extended Langmuir equation.

The objective of the present work was to develop a new approach to correct for the presence of the minor gases in calculating the adsorbed methane in shale, using the parameters that efficiently determined by HS-GC. The main focuses were on the error analysis of the Langmuir equation for calculating the adsorbed gas and the derivation of the conversion of adsorption equilibrium partition coefficients to adsorption constants in the Langmuir equation. The derived relationship was tested by application to a case study of calculating the content of adsorbed methane in a shale sample.

2. Experimental

2.1. Samples

The shale samples were obtained from shale gas reservoir in both China (sample A and B) and North America (sample C). Each sample was ground and screened to 60–80 mesh; the average particle size was 214 μm . The key information, including specific surface area, Langmuir constant, adsorption equilibrium partition coefficient, and maximal adsorbed gas, were obtained from analysis of core samples using BET method, the Langmuir isothermal adsorption test and the HS-GC methods.

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) and an automatic headspace sampler (DANI HS 86.50, Italy) were used for HS-GC measurement.

3. Results and discussion

3.1. Error analysis

When the Langmuir volume (G_{al}) and pressure (p_L) of analyte(s) in the Langmuir equation, i.e., Eq. (1), are available, the volume of the adsorbed analyte(s) (G_a) at any pressure can be calculated. According to Eq. (1) and the propagation of uncertainty (or propagation of error) [19], the uncertainty of G_a (as relative standard deviation, RSD) can be expressed as

$$\text{RSD} = \frac{s_{G_a}}{G_a} = \sqrt{\left(\frac{\partial \ln G_a}{\partial G_{al}} \right)^2 s_{G_{al}}^2 + \left(\frac{\partial \ln G_a}{\partial p_L} \right)^2 s_{p_L}^2 + \left(\frac{\partial \ln G_a}{\partial p} \right)^2 s_p^2} \quad (3)$$

All symbols and definitions are listed in Table 1. Combine Eqs. (1) and (3) to have

$$\text{RSD} = \sqrt{\left(\frac{1}{G_{al}} \right)^2 s_{G_{al}}^2 + \left(\frac{1}{p + p_L} \right)^2 s_{p_L}^2 + \left(\frac{p_L}{p(p + p_L)} \right)^2 s_p^2} \quad (4)$$

Thus, it can be seen from Eq. (4) that the error in the G_a measurement is a function of G_{al} , p_L , and the pressurized pressure (p). Adopting the permitted uncertainties (i.e., 10%) in both G_{al} and p_L measurement from Langmuir isotherm experiment and a margin of error of 0.01 MPa for the pressure [20], the standard errors (i.e., $s_{G_{al}}$, s_{p_L} , and s_p) for G_{al} , p_L , and p can be determined. Thus, the RSD of the Langmuir isotherm experiment at various pressures can be estimated using Eq. (4). The relationship between the RSD and the pressurized pressure is shown in Fig. 1.

As shown in Fig. 1, the Langmuir isotherm experiment can provide a good measurement precision at higher pressure range, indicating that it is suitable to be used for the determination of the major gas (i.e., methane) at the subterranean pressure. However, a significant error can be expected when the Langmuir isotherm experiment is used for measuring the amount of a minor gas, such

Table 1
Symbols and definitions.

Symbols	Definitions	Units
a	Specific surface area	m^2/g
b	Adsorption constant	MPa^{-1}
C_a	Gas concentration in the adsorbed phase	$\text{g}(\text{gas})/\text{m}^2$
C_g	Gas concentration in the vapor phase	$\text{g}(\text{gas})/\text{mL}$
G_a, G_{al}	The adsorbed gas content and the Langmuir volume of gas, respectively	m^3/t
G_a^{Me}, G_{al}^{Me}	The adsorbed methane and the Langmuir volume of methane, respectively	$\mu\text{mol}/\text{g}$
K_d	Adsorption equilibrium partition coefficient	$(\text{g}/\text{m}^2)/(\text{g}/\text{mL})$
M	Molecular weight of the gas species	$\text{g}(\text{gas})/\mu\text{mol}$
N	Maximal amount of adsorbed gas	$\mu\text{mol}/\text{g}(\text{sample})$
p_L, p_L^{Me}, p_L^i	Langmuir pressure of universal gas, methane and the minor gases	MPa
p	Formation pressure	MPa
R	Molar gas constant	$\text{J}/\mu\text{mol K}$
$s_{G_a}, s_{G_{al}}$	Standard error of adsorbed gas and Langmuir volume, respectively.	$\mu\text{mol}/\text{g}(\text{sample})$
s_{p_L}, s_p	Standard error of Langmuir pressure and pressure, respectively	MPa
T	Temperature	K
y_{Me}, y_i	Molar fraction of methane and minor gases in shale gas, respectively	
θ	Fraction of coverage of shale pore surface by adsorbed gas	%

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