

Article

Comparison of Gravimetric Determination of Methane Sorption Capacities of Coals for Using Their Results in Assessing Outbursts in Mines

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Abstract: The gravimetric method for determining coal gas sorption has many advantages and limitations. The article presents the influence of various factors on the results of methane sorption on coal. In mining practice, in addition to sorption properties of coal, knowledge of methane sorption capacity and effective diffusion coefficient determined when assuming a unipore sorption/desorption model are crucial for predicting sudden releases of methane from coal seams to a mine ventilation environment. In Poland, determining sorption capacities of coals for methane is mandatory when starting mining operations in new parts of coal deposits threatened by outbursts. Traditionally, gravimetric microbalances, such as intelligent gravimetric analysis (IGA), are used to determine adsorption capacity and desorption rate. Recently, newer microbalances XEMIS have been introduced to the market. Two gas laboratories, AGH in Krakow and CLP-B in Jastrzebie-Zdroj, respectively, compared experimental adsorption isotherms using XEMIS microbalances with mutually exchanged coal samples. Both sorption capacity at the pressure of 1 bar (a_{1bar}) and effective diffusion coefficient (D_e) were independently determined for the coal samples tested. The results obtained are comparable despite the use of different microbalance XEMIS models. The conducted studies and comparative evaluation of the results allowed for assessing procedures for determining sorption properties using XEMIS microbalances. The exchange of laboratory experiences also allowed for the identification of methodology factors crucial for the development of a uniform procedure for conducting similar studies with XEMIS microbalance. The proposed factors for testing the sorption behavior of methane in coal structures may be helpful in mining practice.

Keywords: gas disaster prevention and control; gas and coal outburst; sorption properties of coal; sorption isotherm; sorption capacity; effective diffusion coefficient



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1. Introduction

The presence of methane in coal mines poses serious life-threatening risks, particularly in relation to gas explosions and gas and coal outbursts. Gas and rock outbursts belong to the most dangerous hazards in the Polish and global coal mining sectors [1–4], primarily due to their difficulties in recognizing and forecasting [5,6]. Reaching coal seams located at greater depths, which are usually characterized by higher methane content, lower gas permeability, and higher gas sorption capacity, contributes to an increased outburst risk [7,8].

While there has been progress in understanding and addressing methane-related threats, incidents related to methane hazards and gas and rock outbursts continue to occur in Polish hard coal mines, frequently with catastrophic consequences [9,10]. Given the strategic importance of bituminous coal, particularly coking coal for the steel industry, it is

crucial to prioritize underground working safety and continually seek new methods for forecasting and assessing mine operational safety.

Research on methane sorption on coal is one of the main factors in preventing outburst accidents and achieving safe coal mining. At the same time, it allows an increase in the efficiency of methane drainage systems in coal mines [11,12], which may contribute to the development of the dual-resource mine concept, allowing for safe and economical coal and coalbed methane (CBM) coupling coordinated exploitation [13].

In Polish mining practice, recognition of gas and coal outburst hazards is based on several fundamental factors, such as methane content, volatile matter content, coal firmness coefficient, gas desorption index, and drill cutting yield. Symptoms or effects of stress relief during mining and events related to the occurrence of similar phenomena are also taken into account [14,15].

The primary parameter considered in categorizing the risk of gas and coal outbursts is methane content of coal. The procedure for determining methane content of coal is described in the national standard [16]. Its value from $4.5 \text{ m}^3/\text{t}^{\text{daf}}$ and above, while other factors are present, may indicate the existence of this hazard. In this hazard's highest (II and III) categories, the limit methane content is above $8.0 \text{ m}^3/\text{t}^{\text{daf}}$ [15]. The second parameter determining hazard categorization is coal hardness. In the Polish mining industry, hardness is described by Protodiakonov coefficient f , and its value below 0.3 is considered one of the main factors of increased risk of gas and coal outbursts [15,17]. Another parameter is the desorption index, describing the intensity of methane release from coal cuttings [18]. The value indicating danger is 1.2 kPa [15,19,20]. If the desorption index exceeds 2.0 kPa, driving a heading in a coal seam is stopped.

More and more attention is being paid to identifying the sorption properties of coal [3], when recognizing the hazard of methane and coal outbursts. In Poland, identifying sorption capacities is obligatory when working in new parts of a coalbed in mines where the risk of methane and coal outbursts is high [15]. Authorized appraisers, including laboratories with the status of appraisers, are responsible for the method of conducting tests, equipment used, and interpretation of the results. Therefore, differences in methodologies, equipment used, and interpretation of results are unduly tolerated. Nevertheless, it is essential to develop standard, unified procedures/methodologies so that the results of tests conducted by different laboratories are comparable and, most importantly, allow for the appropriate interpretation of the scale of methane-related threats in mining workings.

Many studies have been conducted on the sorption behavior of methane in coal structure; however, many of them encompass coal properties such as virgin coal temperature, maceral composition, moisture content, particle size, and pore morphology in relation to methane sorption on coal [21].

Previous experience shows that, in addition to sorption isotherm of methane on coal, sorption capacity and effective diffusion coefficient [4,22,23] is most important. They are critical parameters that determine the ability of coal to slowly or suddenly release methane. Sorption capacity is defined as gas (CH_4) volume sorbing onto coal in given pressure and temperature conditions. In Poland, for the current prevention of gas and coal outbursts, the sorption capacity of coal is determined at the pressure of 1 bar, close to atmospheric pressure. It refers to the mass of coal without moisture and ash (so-called dry and ash-free coal substance). The critical value defining poorly sorbing coals in mining practice is sorption capacity below $1.5 \text{ g}/\text{cm}^3$ [19,24]. Research shows that the sorption capacity of coal is influenced by factors such as ash content, humidity, degree of coal oxidation, vitrinite content, and composition of macerals [25,26]. Coals characterized by high porosity, easily accessible pore structure, large specific surface area, low level of metamorphism, and high oxygen content are characterized by higher sorption capacities [27]. Moisture in coal samples can particularly influence sorption capacity, with residual moisture playing a dominant role in influencing sorption capacity [28].

Another important parameter influencing the kinetics of methane sorption and desorption is the effective diffusion coefficient (D_e) of methane in coal. The effective diffusion

coefficient is understood as the movement of gas molecules under the influence of their concentration gradient. This coefficient allows you to determine the kinetics of coal's gas absorption/release process. The diffusion coefficient takes into consideration factors such as activation energy of a diffusion process, intermolecular sorption interactions, coal microstructure, and physical properties of methane [22]. Understanding a diffusion process is essential for predicting methane release from coal over time [29]. In Poland, coals are considered prone to outbursts when the value of this parameter is higher than $1.5 \times 10^{-9} \text{ cm}^2/\text{s}$. A higher dynamics of movement of gas molecules is observed in coals with damaged structures. In zones close to geological disturbances, the effective diffusion coefficient reaches relatively high values, above $8.0 \times 10^{-9} \text{ cm}^2/\text{s}$ [19,30–32].

The technique of determining a sorption isotherm is also essential when determining sorption capacity and diffusion coefficient. Two different techniques are commonly used in this regard. These techniques are related to two methods, i.e., manometric-volume and gravimetric. The first method involves recording the amount of gas absorbed through pressure readings (manometric method) or pressure and volume readings (volumetric method), and it requires a very accurate determination of cells and void volumes [33]. In the gravimetric method, the amount of gas absorbed is measured at constant pressure using a highly accurate balance, with a sample suspended mechanically or by magnetic coupling across the wall of a high-pressure vessel [33]. This method is most often used to determine sorption properties of coals in Polish underground mines. The gravimetric method enables the determination of sorption capacity and effective diffusion coefficient for different coals, helping to understand their sorption behavior [23].

However, the gravimetric method for determining methane sorption on coals has several disadvantages. This method requires a complex experimental setup to account for temperature gradients and thermal expansion, which can result in systematic errors [34]. The method may not separate accurately the mechanisms of gas uptake, such as adsorption and absorption [35]. The accuracy and reproducibility of the method can be influenced by a pressure and temperature range, as well as coal's rank [36]. Therefore, it is essential to select the drying temperature to avoid a shrinkage effect of the pore structure due to moisture loss on methane adsorption [37–39].

Other critical mistakes involve inaccuracies in determining the volume and density of coal samples, insufficient equilibration, improper buoyancy corrections, and gas purity issues. Careful attention to these factors is crucial for obtaining reliable methane sorption data using the gravimetric method. However, there is an additional factor that Wang et al. [40] paid attention to. There is a lack of clear guidelines on properly conducting and reporting gravimetric methane sorption measurements on coal. Inconsistent practices in sample preparation, equilibration times, data analysis, and reporting make it difficult to compare results across laboratories.

In Poland, tests of methane sorption capacity on coals are carried out mainly using gravimetric methods for mining practice. So far, gravimetric microbalance IGA (Intelligent Gravimetric Analyzer) systems have been most widely used. XEMIS systems have recently been used. The research objective of this study is to check the results obtained for methane sorption capacity on coals and effective diffusion coefficient D_e using XEMIS analyzers in two laboratory units.

The Gas Laboratory of AGH University in Krakow (AGH) and CLP-B Laboratory in Jastrzebie-Zdroj (CLP-B) decided to compare each other to determine sorption capacity and effective diffusion coefficient based on mutually provided coal samples. Each laboratory tested six coal samples—three of their own and three from the partner's. The research performed and comparative assessment of the results allowed for evaluating the procedures for determining sorption capacities when using the results for assessing methane explosion hazards or outbursts in mines. The mutual exchange of information about the sorption capacities procedure also allowed for identifying key factors that should be clarified to develop a uniform procedure for using the results in mining practice.

2. Premises for Interlaboratory Comparison

The sorption capacity of Polish coals has so far been commonly performed using an IGA apparatus by Hiden Isochema, which stands for isothermal gravimetric analysis. The IGA-001 has usually been considered a proper device for measurements of sorption capacity and diffusivity [24,41,42]. CLP-B is one of the laboratories that has experience in using an IGA system. In 2019, a new generation of XEMIS-001 microbalance by Hiden Isochema came into use. A microbalance and sampling suspension system differ from IGA-001 in design.

The XEMIS-100 device was also launched in 2021 at AGH. Preliminary research conducted by CLP-B comparing the results obtained for the same coals, under the same test conditions, in IGA and XEMIS showed high similarity in the course of experiments and results obtained. However, some changes in the course of the experiment were observed. Figure 1 shows the course of an example experiment for IGA and XEMIS analyzers for samples prepared in the same coal. The same research procedure was applied during both experiments. The most tremendous changes were observed in the initial stage of the experiment, after pressure was set to 1 bar. The course of the experiment also differed when the pressure in the reactor was changed. During individual stages of the test, changes in the sample mass were also noticeable, especially in the IGA apparatus, after setting the pressure to 5 bar.

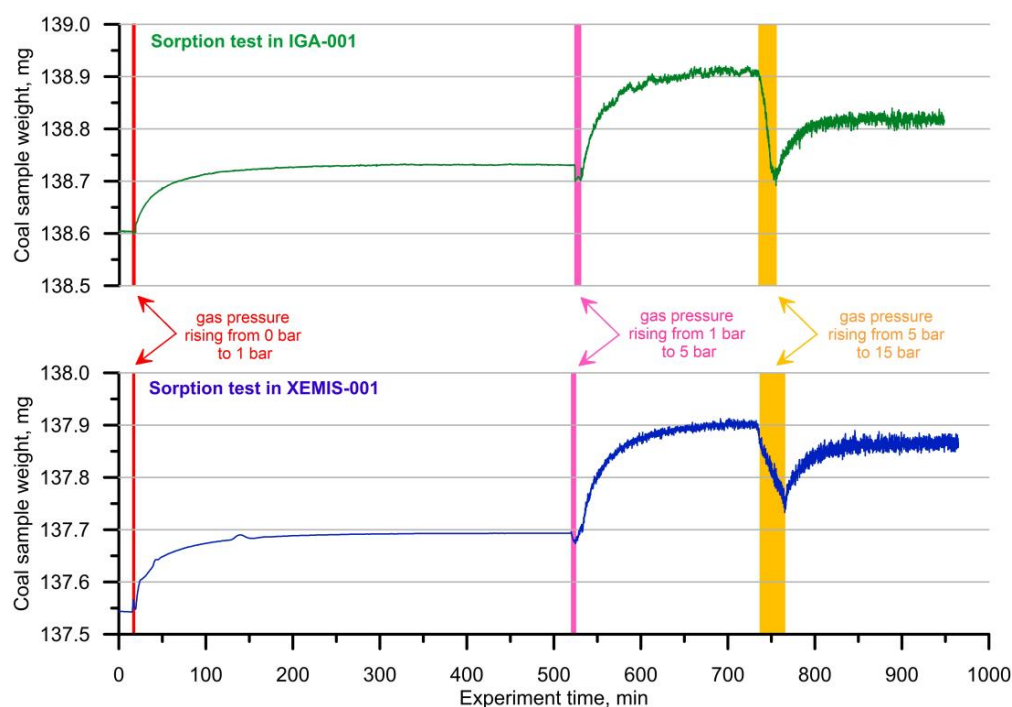


Figure 1. Comparison of mass change for an example coal sample in IGA and XEMIS analyzers during methane saturation.

The observed differences in the measurement results obtained in CLP-B, and the launch of a new XEMIS system at AGH, became the basis for conducting interlaboratory tests by means of two XEMIS devices. A decision was taken to compare sorption properties (sorption isotherm, sorption capacity, and effective diffusion coefficient). AGH also uses the XEMIS-100 device, which differs in configuration from the XEMIS-001 used in CLP-B. The main difference between XEMIS-100 and XEMIS-001 is the operation of a five-gas line, including corrosive gases. The interlaboratory research was aimed at determining the comparability and reproducibility of the results when determining the methane sorption behavior of coals using the gravimetric method, following the research methods used by the participants. Initial arrangements between the laboratories were aimed at developing

standard methodology for determining effective diffusion coefficient and experimental adsorption isotherms for assessment of methane sorption capacity.

3. Materials and Methods

3.1. Characteristics of Gas Sorption Analyzers and Methodology for Determining Sorption Properties

Table 1 presents the basic differences between gas sorption analyzers in two laboratories, AGH and CLP-B, respectively. Figure 2 presents a diagram showing the structure of the XEMIS analyzer.

Table 1. Information on experimental parameters of gas sorption analyzers.

Parameter	AGH	CLP-B
Type of analyzer	XEMIS-100	XEMIS-001
Design pressure range	$1 \times 10^{-6} \div 170$ bar	$1 \times 10^{-6} \div 150$ bar
Pressure transducer ranges	$0 \div 200$ bar $0 \div 100$ mbar $0 \div 1$ bar $0 \div 50$ bar	$0 \div 200$ bar $0 \div 50$ bar $0 \div 1$ bar $0 \div 100$ mbar $0 \div 10$ mbar
Temperature measurement range	$-196 \div 500$ °C	$-270 \div 500$ °C
Temperature accuracy	± 0.1 K	± 0.1 K
Balance capacity	5 g	5 g
Weighing resolution	2×10^{-6} of sample mass	$0.2 \mu\text{g}$ (100 mg) $2 \mu\text{g}$ (1 g)
Long-term weighing stability (24 h cycle in an inert atmosphere at room temperature):	$\pm 5 \mu\text{g}$	$\pm 5 \mu\text{g}$
Short-term weighing stability	$\pm 1 \mu\text{g}$	$\pm 1 \mu\text{g}$
Dynamic weighing range	$0 \div 200$ mg	$0 \div 200$ mg
Long-term pressure stability	$< \pm 0.08$ bar	$< \pm 0.08$ bar
Precision of pressure measurement for the entire measurement range	0.01 bar	0.01 bar
Cabinet (balance) temperature stability	0.1 °C	0.1 °C
Measurement modes	static/dynamic	static/dynamic
Number of connected gas lines	5 (CH_4 , H_2 , CO_2 , N_2 , and corrosive gas)	1 (CH_4)
Operating scope of flow controllers	$20 \div 1000$ mL/min	$20 \div 2000$ mL/min
Accuracy of active pressure regulation	$\pm 0.02\%$ of the range	$\pm 0.02\%$ of the range
Precision of pressure measurement	$\pm 0.04\%$ of the transmitter measurement range.	$\pm 0.02\%$ of the transmitter measurement range
Reactor temperature control systems	Sample 500 °C furnace and controller ($40 \div 500$ °C), Refrigerated recirculating bath ($0 \div 80$ °C), Liquid Dewar Vessel (-196 °C)	Sample 500 °C furnace and controller ($40 \div 500$ °C), Refrigerated recirculating bath ($0 \div 90$ °C)
Valve control	Pneumatic	Mechanical
Additional equipment	Vapor generator, Mass spectrometer	-
Gas CH_4 purity	99.999%	99.995%

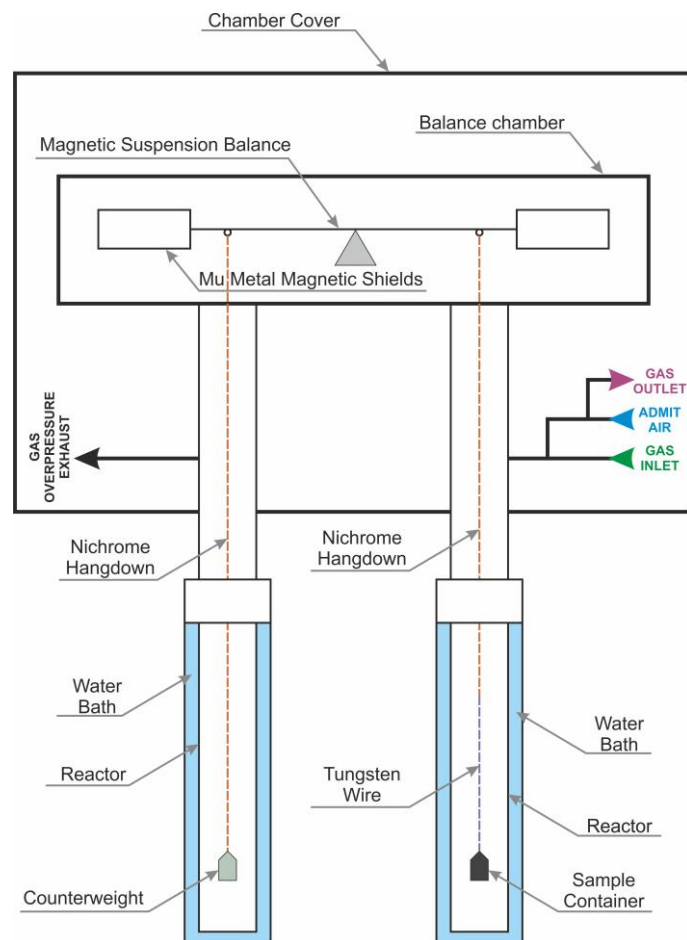


Figure 2. Schematic diagram of microbalance XEMIS.

There are no significant differences between these two types of XEMIS that could affect the differences in the results of methane sorption determination on the tested coal samples.

3.2. Coal Samples Preparation and Experiment Setup

Both AGH and CLP-B laboratories independently collected three coal samples from various Polish underground mines. Due to comparative tests, the laboratories encoded some information regarding coal samples (name of the mine, coal seam number, place of collecting coal samples, etc.). The submitted samples were marked with individual labels of each laboratory's comparison participant. The labels were attached to the tight packaging of the packed samples and sent to a comparison laboratory. The label of the research samples included a participant's code number and an individual designation of the research object. For the first laboratory, the code is AGH, and for the second one, the code is CLP-B. AGH provided three samples with codes AGH 1, AGH 2, and AGH 3. CLP-B provided three samples with codes CLP-B 1, CLP-B 2, and CLP-B 3.

In places where coal samples were collected for testing, measurements of additional parameters important in mining practice and recognizing gas and rock outbursts were taken. The following parameters were determined: virgin rock temperature, methane content of coal, coal hardness, and desorption intensity index. The parameters are listed in Table 2.

Table 2. Coal parameters at the place where samples were collected.

No.	Coal Sample Determination	Virgin Rock Temperature	Methane Content of Coal	Protodiakonov's Coefficient of Coal Hardness	Desorption Intensity Index	True Density	Ash Content
		VRT	M_n	f	dp	ρ_s	A_a
		°C	m ³ /t daf	-	kPa	kg/m ³	%
1	AGH 1	38.0	4.356	0.42	0.85	1.320	6.56
2	AGH 2	45.5	3.215	0.39	1.32	1.328	5.49
3	AGH 3	47.0	6.241	0.35	0.98	1.355	8.20
4	CLP-B 1	37.0	3.131	0.40	0.42	1.351	4.91
5	CLP-B 2	39.4	8.740	0.38	1.46	1.325	1.18
6	CLP-B 3	45.0	7.708	0.34	1.22	1.369	5.25

A given laboratory prepared samples. However, a joint sample preparation method for testing was determined. Coal samples were ground and sieved to obtain a fraction ranging from 0.16 to 0.20 mm. Next, coal parameters necessary for conducting sorption tests were determined. The following parameters were established for the samples: ash content, true density of coal. The results of these studies are summarized in Table 2.

Although both laboratories have similar procedures for determining methane sorption on coal samples, there are some differences in the selected stages of sample testing. This is due to organizational reasons in both laboratories. AGH laboratory conducts adsorption tests over a more extended period of the pretreatment stage. Due to other obligations and equipment use, CLP-B laboratory completes this stage in a shorter period of time. The main differences in the procedures concern temperature and time of pretreatment stage in XEMIS, number of isotherm points, and process registration time under given pressure conditions. Differences in the procedure for testing coal samples are presented in Table 3.

Table 3. Procedure comparison of coal sample testing by XEMIS analyzers.

Stage	Parameter	AGH	CLP-B
Pretreatment	Sample temperature, °C	45	85
	Duration, min	720	240
	Coal sample weight, mg	130 ± 5	135 ± 5
Test conditions for determining both sorption capacity at the pressure of 1 bar and effective diffusion coefficient	Sample temperature, °C	According to VRT at the place of sampling (see Table 2)	
	Gas pressure, bar	1.0	
	Duration, min	1080	
Test conditions for determining sorption isotherm parameters	Number of isotherm points	5	3
	Gas pressure (sorption), bar	1.0/3.0/5.0/10.0/15.0	1.0/5.0/15.0
	Duration (sorption), min	1080 for each point	1080/800/500
	Gas pressure (desorption), bar	1.0	5.0/1.0
	Duration (desorption), min	1080	1000/1000
Conversion of results into established conditions	Pressure, Pa	100,000	
	Temperature, °C	25.0	

A change in a sample weight during methane sorption is influenced by buoyancy, which should be carefully corrected. Proper correction of buoyancy effect is always necessary when using a gravimetric method for testing gas sorption on coals. As pressure increases, buoyant force on the sample increases, causing a visible decrease in mass [43]. While recording the measurements, displacement corrections related to a change in methane density under given pressure and temperature conditions were made.

3.3. Application of Sorption–Desorption Method

Based on the findings, interlaboratory comparisons were planned to determine sorption isotherms, which would then be used to determine sorption capacity and effective diffusion coefficient.

Despite the limitations of the uniport diffusion model [33,44], previous studies on methane sorption on coals in Poland [7,45] confirm that its use is sufficient. Therefore, diffusion in coal, according to Fick's equation and the uniport diffusion model with varying spherical grain size, is taken into account, which takes the following form:

$$\frac{\delta c(r, t)}{\delta t} = \frac{D}{1 + H} \cdot \nabla^2 \cdot c(r, t) = D_e \cdot \nabla^2 \cdot c(r, t) \quad (1)$$

where c is the total gas concentration in mol/m^3 , r is the distance from the center of the grain in m, t is the time in seconds, D is the diffusion coefficient in m^2/s , D_e is the effective diffusion coefficient in m^2/s , $D_e = \frac{D}{1+H}$, and H is the slope coefficient in Henry's adsorption isotherm in $\text{m}^3/(\text{g} \cdot \text{bar})$.

The literature widely describes the solution to Equation (1) taking into account boundary conditions and initial conditions [7,46]:

$$\frac{a(t)}{a_m} = 1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \left[\frac{1}{n^2} \cdot e^{\left(-\frac{n^2 \cdot \pi^2 \cdot D_e \cdot t}{R^2}\right)} \right] \quad (2)$$

where $a(t)$ is the amount adsorbed gas after time t in cm^3/g , a_m is the maximum amount of adsorbed gas at equilibrium state in cm^3/g , n is the integer—number of series terms ($n \geq 1$), t is the time in seconds, and R is the substitute grain radius in cm.

The above unipore diffusion model was chosen for kinetic modeling study and diffusion coefficient determination. The presented Formula (2) shows that, with a constant grain class, time dependence of the accumulation or desorption of methane from a coal sample depends on target methane content in the sample under given pressure and temperature conditions (final mass of the sample) and diffusion coefficient D_e .

To determine the effective diffusion coefficient, Formula (3) given by Timofeev [31] for the half-time of the sorption process, which is commonly used in this type of consideration, was used [7,46]:

$$D_e = \frac{0.308 \cdot R^2}{\pi^2 \cdot t_{1/2}} \quad (3)$$

where R is the substitute grain radius in cm, and $t_{1/2}$ is the half-time of the sorption process in seconds.

The substitute grain radius is calculated using the following formula:

$$R = \frac{1}{2} \sqrt[3]{\frac{2 \cdot d_1^2 \cdot d_2^2}{d_1 + d_2}} \quad (4)$$

where d_1 and d_2 are the lower and upper limits, respectively, of grain diameter in the coal sample in centimeters.

Based on the measurements taken, Langmuir sorption isotherms were determined according to Equation (5):

$$a = a_m \cdot \frac{b \cdot p}{1 + b \cdot p} \quad (5)$$

where a is the methane adsorbed at pressure p in $\text{cm}^3/\text{g}^{\text{daf}}$, p is the equilibrium pressure of methane in bar, a_m is the maximum monolayer volumetric capacity in $\text{cm}^3/\text{g}^{\text{daf}}$, b is the Langmuir constant in $1/\text{bar}$.

The methane sorption capacity $a_{1\text{bar}}$ was determined at equilibrium pressure of 1 bar.

4. Results and Discussion

Table 4 presents the obtained results of fitting the Langmuir isotherm, determined sorption capacity a_{1bar} , and effective diffusion coefficient D_e . Both laboratories presented these parameters separately for all tested coal samples.

Table 4. Results of fitting the Langmuir model and determining a_{1bar} and D_e .

No.	Coal Sample Determination	Sorption Capacity at the Pressure of 1 bar		Effective Diffusion Coefficient		Coefficients of Langmuir Model Fitting				Coefficient of Determination for Langmuir Model Fitting	
		a_{1bar}		D_e		a_m		b		R^2	
		$\text{cm}^3/\text{g}^{\text{daf}}$		$\times 10^{-9} \text{ cm}^2/\text{s}$		$\text{cm}^3/\text{g}^{\text{daf}}$		$1/\text{bar}$			
		AGH	CLP-B	AGH	CLP-B	AGH	CLP-B	AGH	CLP-B	AGH	CLP-B
1	AGH 1	2.71	2.84	1.44	1.42	21.34	18.32	0.130	0.168	0.9990	0.9972
2	AGH 2	2.19	2.46	1.31	1.36	20.39	18.12	0.109	0.145	0.9993	0.9982
3	AGH 3	1.99	2.13	1.01	1.07	19.02	17.01	0.105	0.134	0.9990	0.9978
4	CLP-B 1	2.72	2.74	1.02	1.23	20.44	19.31	0.139	0.156	0.9992	0.9993
5	CLP-B 2	1.83	1.87	0.26	0.30	16.16	14.45	0.120	0.144	0.9995	0.9996
6	CLP-B 3	2.20	2.36	1.85	1.67	20.37	18.45	0.110	0.146	0.9995	0.9978

A preliminary analysis of these results indicates their high convergence. It should be borne in mind that the procedures of both laboratories included differences in the procedure of the pretreatment test. Despite a shorter heating time, preparing samples at a higher temperature was probably more effective in obtaining a higher value of sorption capacity a_{1bar} in each case of determinations made in CLP-B. This confirms the researchers' conclusions that effective moisture removal from a sample significantly increases sorption capacity [28].

When comparing effective diffusion coefficient D_e , it can be noticed that slightly higher values for some samples were obtained in the AGH laboratory and others in the CLP-B laboratory. The largest difference between the values was $0.21 \times 10^{-9} \text{ cm}^2/\text{s}$ (sample CLP-B 1) and the next $0.18 \times 10^{-9} \text{ cm}^2/\text{s}$ (sample CLP-B 3). The remaining value differences were less than $0.07 \times 10^{-9} \text{ cm}^2/\text{s}$. The results of these comparisons can be considered repeatable. Therefore, the results should be regarded as convergent and sufficiently accurate for mining practice.

Table 5 shows the difference between test results related to mean value determined by both laboratories. In half of the cases, the differences in determinations of sorption capacity a_{1bar} related to the average do not exceed 5%. Only in one case did this difference exceed 10%. In the case of effective diffusion coefficient D_e , the discrepancy between measurement results and the average is greater. In two cases, it did not exceed 5%; in one, it was close to 20%. In other cases, it remained within the range of 5–20%.

Table 5. Differences in results from the average values.

No.	Sorption Capacity at the Pressure of 1 bar				Coefficients of Langmuir Model Fitting			
	a_{1bar}				D_e			
	$\text{cm}^3/\text{g}^{\text{daf}}$				$\times 10^{-9} \text{ cm}^2/\text{s}$			
	AGH	CLP-B	Average	Difference from the Average	AGH	CLP-B	Average	Difference from the Average
1	2.71	2.84	2.775	4.7%	1.44	1.42	1.430	1.4%
2	2.19	2.46	2.325	11.8%	1.31	1.36	1.335	3.7%
3	1.99	2.13	2.060	6.9%	1.01	1.07	1.040	5.8%
4	2.72	2.74	2.730	0.7%	1.02	1.23	1.125	18.7%
5	1.83	1.87	1.850	2.2%	0.26	0.30	0.280	13.1%
6	2.20	2.36	2.280	7.1%	1.85	1.67	1.760	10.2%

Figure 3a–f show the comparison of sorption isotherms determined in both laboratories. The graphs show isotherm data determined from the measurement results (5 points at AGH and 3 points at CLP-B) and the fitting results obtained using the Langmuir sorption isotherm equation (Equation (5)). The experimental results $a = f(p)$ were approximated by Equation (5) using the least square method to determine a_m and b . The fitting of the Langmuir curve is appropriate, as indicated by R^2 values. The calculated R^2 values are presented in Table 4. The courses of sorption isotherms are very similar, practically within the range of analyzed pressures, up to 15 bar. However, in four cases, R^2 is higher for the procedure in AGH (coal samples AGH 1, AGH 2, AGH 3, CLP-B 3) than for the procedure in CLP-B. In the other two cases, the R^2 coefficient differs by only 0.0001. Fitting the Langmuir sorption isotherm based on the five measurement points seems more advantageous.

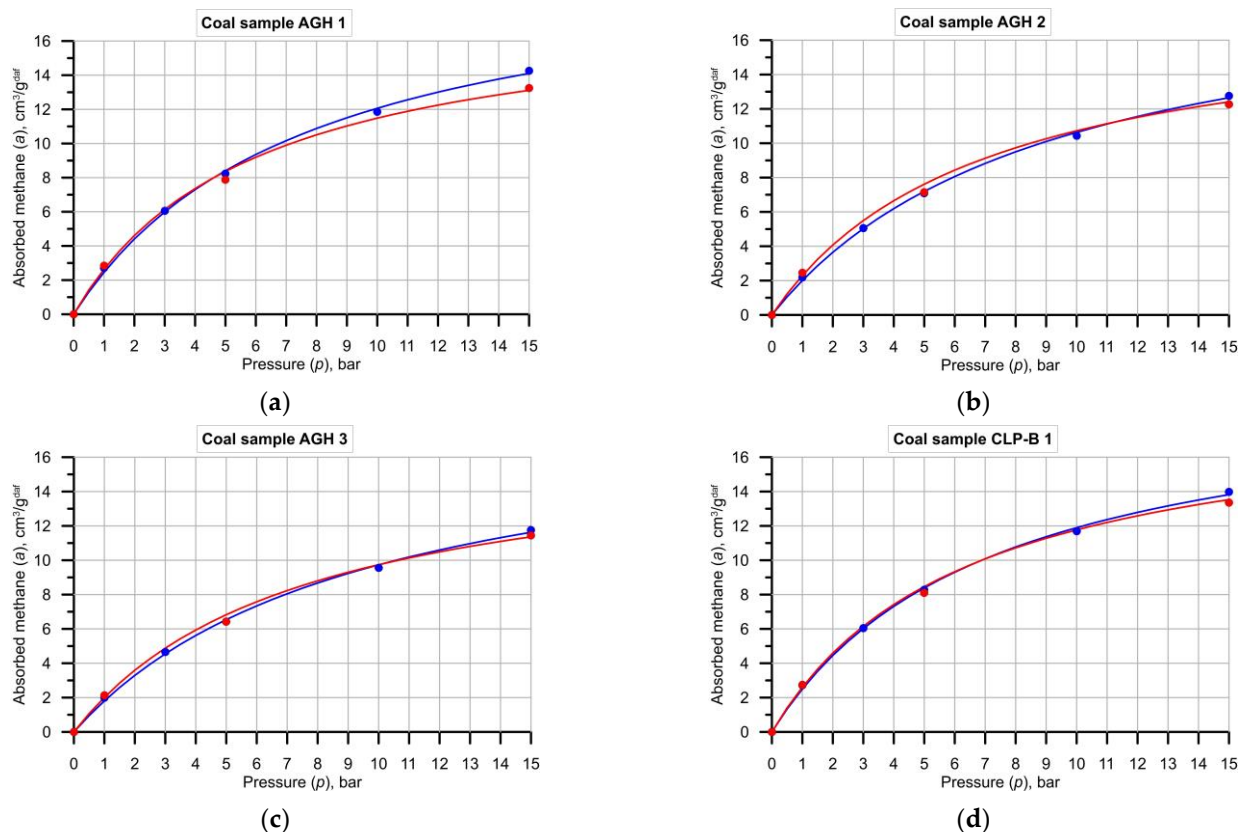


Figure 3. Cont.

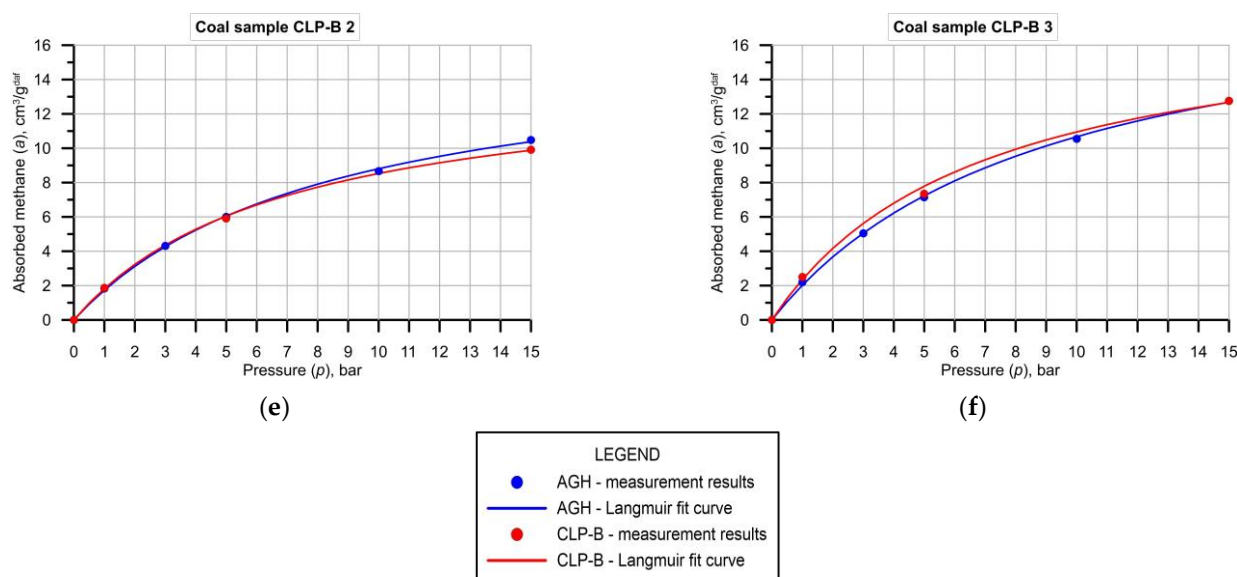


Figure 3. Methane adsorption isotherms for tested coal samples: (a) Coal sample AGH 1; (b) Coal sample AGH 2; (c) Coal sample AGH 3; (d) Coal sample CLP-B 1; (e) Coal sample CLP-B 2; (f) Coal sample CLP-B 3.

For each of the analyzed results of AGH samples 1–3, it can be noticed that isothermal curves tend to have a higher maximum sorption capacity value, which is confirmed by charts and results of a_m values in Table 4. In the case of determining sorption isotherms, it seems reasonable to conduct measurements for a larger number of points to increase the accuracy of its determination.

The comparative measurements showed similar results, when considering some factors influencing the determination of searched values of sorption capacity at pressure of 1 bar (a_{1bar}) and effective diffusion coefficient (D_e) for coal samples tested. The differences in results may be related to:

- differences in masses of tested samples in both laboratories;
- differences in pretreatment procedure of coal samples in XEMIS analyzers;
- inaccuracies in reading a set sorption filling when determining diffusion coefficient;
- in the case of sorption isotherms, the differences may also be related to a number of determinations of adsorbed gas for isotherms determined using the Langmuir model.

Moreover, higher values of sorption capacity were obtained at pressure of 15 bar in AGH laboratory. This may be due to a longer gas saturation time of coal samples at higher pressures during tests in AGH laboratory than in CLP-B laboratory.

Other factors, such as those related to types of XEMIS microbalances, should not affect the results of sorption capacity determinations if constant laboratory conditions are maintained and are consistent with the requirements for the correct installation and operation of the analyzer.

Nevertheless, the research allows conclusions to be drawn on the basis of the results of sorption efficiency measurements in coal mines. The obtained results of interlaboratory comparisons prove their high convergence. The precision of determining values (a_{1bar}) and (D_e) in both laboratories is sufficient to use them in recognizing methane behavior in coal seams and predicting gas and rock outbursts [4,17,18]. Determining sorption isotherms and determining sorption capacity at pressure of 1 bar (a_{1bar}) and effective diffusion coefficient (D_e) may help to determine places particularly exposed to gas-geodynamic phenomena. However, the measurements should be carried out according to established and comparative research methodology because only such an approach

guarantees a proper comparison of subsequent results. The selection of test conditions and equipment is crucial for the reliability of the results. Therefore, essential factors of a

unified procedure for determining methane sorption on raw coal using the XEMIS analyzers are recommended as follows:

1. Mass and grain size distribution of coal samples should be uniform.
2. Temperature of the pretreatment stage should be determined. Temperature should increase as the stage's assumed duration shortens.
3. For mining practice, the sorption isotherm should be determined for virgin rock temperature of coal on site.
4. Number of methane sorption capacity points within the range of analyzed pressures should be determined. However, it is recommended to exclude the sorption capacity for five values of saturation pressure, of which the first three points should correspond to pressure values of 1, 3, and 5 bar, respectively.
5. Maximum time for saturating the sample with methane should be established.

The factors of methodology above should be verified with a larger number of tests in various laboratory centers. The ongoing research and verification process is crucial for continuously improving and refining our understanding of methane sorption on coal.

Research into determining sorption capacity at pressure of 1 bar (a_{1bar}) and effective diffusion coefficient (D_e) should be conducted for coal samples taken from different locations in the developed coal seam, especially near expected geological disturbances or other indications of outburst risk, such as areas with high methane content or high-stress strata locations. The accuracy of determining a_{1bar} and D_e is a critical area where further research should be conducted.

In mining practice, for the analysis of outbursts, observing the variability of sorption/desorption parameters and methane diffusivity in different places of a coal seam is more important than numerical values of these parameters [4,17]. However, it should be remembered that methane diffusion behavior and sorption/desorption characteristics are among many factors that estimate outburst risk.

5. Conclusions

Based on interlaboratory comparison of sorption capacities of tested coal samples by gravimetric method, the following conclusions can be drawn:

1. Despite the differences in configuration between XEMIS-001 and XEMIS-100 analyzers and procedures in methodology, the methane sorption results obtained on the six coal samples tested in CLP-B and AGH laboratories are very similar. Apart from one case, the deviation from the average value of sorption capacity (a_{1bar}) did not exceed 10%. In the case of effective diffusion coefficient (D_e), the deviation from the average value for the first three samples does not exceed 10%, and for the following three samples, it remained within the range of 10–20%.
2. The most notable discrepancies in the results were observed when matching the Langmuir sorption isotherm. It was found that matching a curve for five isotherm points according to AGH procedure is more beneficial than matching a curve for three points according to CLP-B procedure.
3. Slight differences in the procedures for conducting sorption tests on coal samples may influence the results of comparative tests. Key factors affecting the obtained results are related to temperature and duration of the pretreatment stage, sample saturation time of methane, and number of measurement points for determining the Langmuir isotherm.
4. The proposed essential methodology factors for determining methane sorption on coal by XEMIS analyzers constitute a foundation for developing a unified procedure. Applying the unified procedure is vital for comparing results in mining practice and assessing the risk of outbursts. Further research in this field is necessary to define the procedure in detail.

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