Arch. Min. Sci. **66** (2021), 2, 197-211
Electronic version (in color) of this paper is available: http://mining.archives.pl

DOI 10.24425/ams.2021.137456

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THE INFLUENCE OF NITROGEN INERTISATION ON GRAHAM'S RATIO VALUE

As a preliminary point, four longwalls, where inertisation of goafs using nitrogen was applied, have been characterised. Next, the issue concerning the unreliable Graham's ratio values, which occur in certain ranges of its denominator value, were discussed. The reliability criterion of this indicator was also quoted. Afterwards, a basic statistical sample consisting of the results of chromatographic analyses of air samples taken from longwalls areas, where nitrogen inertisation was not applied and were classified by Graham's ratio as samples safe from endogenous fire hazard was described. Then, the results of comparative analyses of the base sample with the concentrations of gases contained in air samples taken from the areas of the previously described four longwalls, which according to Graham's ratio, were also safe from the endogenous fire were presented. Comparative analyses were performed before and after applying Graham's ratio reliability criterion.

Keywords: mining, fire hazard, Graham's ratio, inertisation

1. Introduction

Graham's ratio has been used for many years to assess the level of endogenous fire hazard during the exploitation of hard coal seams. In the current Minister of Energy Regulation on detailed requirements for the operation of underground mining facilities [12], it is one of the basic criteria used to determine the threat on measuring stations located at longwall goafs and near insulation dams.

Graham's ratio was developed in the period when nitrogen inertisation was not used in hard coal mines – hence the correctness of the assessment according to this indicator was sufficient then. At present, when inertisation became, so to say, an element of hard coal mining technol-

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ogy using a longwall system, it often happens that nitrogen used in inertisation fundamentally disturbs this assessment.

This study presents an analysis of the influence of increased nitrogen concentrations on Graham's ratio values. Its reliability was verified based on the results of precise chromatographic analyses of air samples taken from the areas of longwalls in which nitrogen was used as an inert gas.

2. Characteristics of analysed materials

In order to investigate the influence of increased nitrogen concentrations on Graham's ratio value, the results of precise chromatographic analyses of air samples taken from longwall areas where nitrogen was used as inert gas were obtained. The received data concerned four longwalls carried out in the seams of the group:

– 200 – hereinafter referred to as longwall No. I,
– 400 – hereinafter referred to as longwall No. II,
– 400 – hereinafter referred to as longwall No. III,
– 500 – hereinafter referred to as longwall No. IV.

<u>Longwall I</u>

The longwall I was a longwall with a natural roof caving from the boundaries of the operational field. It was first ventilated using the "U" method with the air inlet and outlet, along the unmined coal and then using the "Y" method with the air outlet in two directions. The thickness of the exploited seam in the parcel of this longwall was on average 2.95 m. In the longwall working goafs coal was left with an average thickness of 0.33 m in the roof and 0.25 m in the sole.

The amount of air ventilating the longwall varied, at different stages of operation, in a range of about 180 m^3/min to 480 m^3/min. The goafs of the longwall I was supplied with nitrogen initially at the amount of 300 m^3/h (5 m^3/min), and then the inertisation intensity was increased up to 600 m^3/h (10 m^3/min).

<u>Longwall II</u>

The longwall II was a longwall with a natural roof caving to the boundaries of the exploitation field, with main gates made before the beginning of the longwall. It was ventilated using the "U" method with the air inlet and outlet along the unmined coal. The thickness of coal in the exploited deck ranged from 3.8 m to 6.3 m (with interlayers of slates and dant).

The amount of air flowing through the longwall ranged from 800 m^3/min to 950 m^3/min. Nitrogen in the amount of 700 m^3/h (11.7 m^3/min) to approximately 1400 m^3/h (23.3 m^3/min) was transported to the goafs of the longwall II.

<u>Longwall III</u>

The longwall III was a longwall with a natural roof caving from the boundaries of the exploitation field, and it was ventilated using the "U" method with the air inlet and outlet along the unmined coal. The average thickness of the exploited deck in the longwall III parcel was 2.65 m (with interlayers of clay slate and dant). Around the middle of the planned longwall length, coal with a thickness of 0.2 m to 0.5 m was left in the bottom.

The amount of air flowing through the longwall varied from about 2000 m^3/min to 480 m^3/min. At various stages of exploitation, nitrogen was supplied in quantities from 600 m^3/h (10 m^3/min) to 1000 m^3/h (16.7 m^3/min) into the goafs of the longwall III.

Longwall IV

The longwall IV was a longwall with a natural roof caving from the boundaries of the exploitation field and ventilated using the “U” method with the air inlet and outlet along the unmined coal. The thickness of coal in the longwall parcel varied from 4.5 m to about 6 m. Coal with a thickness of 0.9 m to 1.2 m was left at the bottom of the longwall excavation.

The amount of air flowing through the longwall was about 700 m^3/min. Nitrogen in the amount of 700 m^3/h (11.7 m^3/min) to about 1350 m^3/h (22.5 m^3/min) was supplied to the goafs of the longwall IV.

In the areas of all the mentioned longwalls, at various stages of operation, there was an increased fire hazard, which according to the Minister of Energy Regulation [12] is characterized, among others, by the Graham index with the following criteria:

- $0 < G \leq 0.0025$ – normal situation – there is no threat in goafs,
- $0.0025 < G \leq 0.0070$ – increased observation of the atmosphere in the goafs, increased frequency of air sampling,
- $0.0070 < G \leq 0.0300$ – work should be undertaken to eliminate or reduce the threat while maintaining normal operations in the affected area, with the work plan being prepared by the Head of the Ventilation Department and approved by the Mine Operator,
- $G > 0.0300$ – fire-fighting action.

The values of Graham’s ratio calculated on the basis of gas concentrations, contained in air samples taken from the goafs of the examined longwalls and from behind the insulation dams, which had contact with these goafs, in many cases exceeded 0.0025. It was also found that the subsequent threshold values of this indicator were exceeded.

Inertisation using nitrogen was used to counteract the fire hazard in goafs of these longwalls. The purpose of this action was to lower the oxygen concentration in the area of coal self-heating. According to Szlązak and Piergies [15], oxygen concentration lower than 8% is safe from the point of view of the self-ignition of coal.

Therefore, air samples from the described areas were an excellent material for investigating the influence of increased nitrogen concentrations on the reliability of the assessment of the endogenous fire hazard level according to Graham’s ratio.

3. Graham’s ratio reliability range

Graham’s ratio is determined according to the formula [12]:

$$G = \frac{\mathrm{CO}}{0{,}265 \cdot \mathrm{N}_2 - \mathrm{O}_2} \tag{1}$$

where:

- CO — concentration of carbon monoxide [%],
- N_2 — nitrogen concentration [%],
- O_2 — oxygen concentration [%].

From the mathematical structure of Graham’s ratio, it follows that the function describing it is going asymptotically to zero or infinity. Therefore, it can be proved that in certain intervals the indicator gives unreliable levels of fire hazard, which is directly related to the value of its denominator.

This problem was described by MacKenzie-Wood and Strang [7], who stated that Graham's ratio denominator lower than 0.2 introduces serious errors and caution should be exercised when interpreting such results.

However, Mitchell [8] and Brady [2,3] noticed that for a denominator value of less than 0.3, Graham's ratio may be unreliable.

Ray et al. [11] also found that Graham's coefficient has disadvantages when oxygen deficiency is less than 0.3.

Moraru and Babut [9] believe that when oxygen deficiency in Graham's ratio is less than 0.3, then the resolution of the measuring device is crucial because every slight variation from true concentrations can cause a problem with determining this ratio.

Muller et al. [10] stated that the optimal, minimum value of the indicator denominator should be in the range of 0.1 to 0.3 – because the rejection of all cases for which this value is less than 0.3 may lead to the loss of potentially important results, for an atmosphere close to atmospheric air.

Cliff [4] wrote that when inertisation is used, care needs to be taken on Graham's ratio interpretation. Inertisation techniques can upset the oxygen deficiency and artificially reduce this index.

Bajic et al. [1] believe that samples with oxygen content close to atmospheric air may result in an incorrect value of oxygen deficiency in the Graham' ratio. A similar problem occurs with samples diluted with seam gas.

In the articles by Słowik and Świerczek [13,14], a 2777 element statistical sample consisting of precise chromatographic analyses of mine air samples was discused. By applying the appropriate mathematical tools, a conclusion was drawn with a probability of at least 95% that if the value of Graham's ratio denominator varies between 0.2 and 5.7, this indicator is reliable. However, if the denominator value is outside the specified range, Graham's ratio values are unreliable, and in such cases, other fire risk assessment criteria should be used. The authors justified their conclusion with examples, in which the very low values of Graham's ratio denominator caused that the indicator generated an erroneously elevated level of fire risk. On the other hand, the high values of this denominator allowed to observe the opposite situation – lowering the level of fire hazard. Therefore, the analysis of the influence of elevated nitrogen concentrations on Graham's ratio value – including the given reliability range – is presented in the further part of this paper based on air samples taken from the longwalls I, II, III and IV, where nitrogen inertisation was applied.

4. Base sample for conducting a comparative analysis of mine air samples

It has been proved – among others in the studies by Słowik and Świerczek [13,14] – that the reliability of the fire hazard level assessment according to Graham's ratio is directly influenced by the value of its denominator. In turn, one of the gases based on which the denominator is determined is nitrogen. It follows that an increase in nitrogen concentration (e.g. as a result of inertisation) may result in lowering the fire hazard level signalled by this indicator. However, incorrect classification (by Graham's ratio) of the air sample as not endangered by fire, where in reality it would represent a higher level of danger, is a highly undesirable situation. That is why, in the further analysis of this problem, only those cases were considered for which Graham's ratio values were in the first range shown in Annex 3 to the Minister of Energy Regulation [12], i.e. they did not exceed 0.0025. The air samples selected in this way (according to the discussed indicator) did not indicate any risk of endogenous fire.

For the purposes of further analysis, the following assumption was made: if Graham's ratio correctly signals that the air samples do not indicate a fire hazard, the concentrations of gases generated in the process of self-heating of coal (such as ethylene, propylene, acetylene, carbon monoxide or hydrogen) – both in the case of samples taken from areas which are not subjected to nitrogen inertisation and samples from areas where nitrogen is used – should be at a similar, low level. Based on this assumption, it was decided to compare the results of chromatographic analyses of air samples taken from areas of longwalls I, II, III and IV which are inerted using nitrogen, with results of air samples taken from areas that are not subjected to inertisation.

For this purpose, in the first step, a basic statistical sample was prepared, which consisted of the results of chromatographic analyses of air samples taken from longwall goafs and from behind the insulation dams, in which nitrogen was certainly not used as an inert gas. From an extensive database containing the results of precise chromatographic analyses of mine air samples (using appropriate queries created in SQL), 36239 cases were selected according to the following criteria:

- air samples had to be taken from longwall goafs or from behind the insulation dams – which is in accordance with applicable regulations [12],
- to eliminate air samples with increased nitrogen content, the concentration of this gas should be less than 80% – this value was assumed because higher concentrations of N_2 are already observed in the initial inertisation phase,
- Graham's ratio value determined on the basis of gas concentrations contained in air samples had to be within the range of $0 < G \leq 0.0025$ – i.e. selected samples represented the fire hazard level described by the regulations as a normal situation [12],
- the value of the Graham's ratio denominator had to be within the range of 0.2÷5.7 – to eliminate the unreliable (overstated and underestimated) values of this indicator [14].

Table 1 presents descriptive statistics for the statistical sample determined in this way.

TABLE 1

Basic statistical sample – without modification

Variable	Descriptive statistics						
	Valid N	**Mean**	**Minimum**	**Maximum**	**Percentile 90**	**Standard deviation**	**Skewness**
Ethylene [ppm]	36239	0.064	0.01	21.20	0.10	0.282	35.580
Propylene [ppm]	36239	0.050	0.01	6.81	0.10	0.133	22.609
Acetylene [ppm]	36239	0.011	0.001	14.000	0.015	0.107	74.646
Carbon monoxide [ppm]	36239	9.132	1	142	22	12.776	3.582
Oxygen [%]	36239	18.639	0.01	20.78	20.66	3.546	–3.360
Nitrogen [%]	36239	75.690	3.19	79.99	79.68	10.866	–4.365
Carbon dioxide [%]	36239	1.156	0.01	94.87	2.08	4.864	12.957
Methane [%]	36239	4.504	0.00	94.08	10.40	12.554	4.491
Hydrogen [ppm]	36239	10.021	0.2	5700.0	13.7	60.769	43.995
Graham's ratio	36239	0.00074	0.00002	0.00255	0.00169	0.00061	1.002
Graham's ratio denominator	36239	1.419	0.20	5.70	3.40	1.264	1.470

While analysing Table 1, it can be concluded that the average concentrations of some gases generated in the process of self-heating of coal (such as ethylene, propylene, acetylene, carbon monoxide and hydrogen) did not show signs of an increased level of endogenous fire hazard [5,16,17]. However, the maximum concentrations of these gases were already significantly higher.

As it is known, the percentile 90 means that 90% of cases from the available statistical sample are less than or equal to the value indicated by this parameter. In this regard, it turned out that at least 90% of the analysed air samples were characterised by much lower concentrations of the abovementioned gases than their maximum concentrations. The concentrations of the analysed gases were characterised by a very high asymmetry to the determined mean. This is confirmed by high skewness values, which is a measure of the asymmetry of the distribution.

All this suggests that the discussed statistical sample contained outliers that were eliminated in the next step by applying the two-sigma rule. Therefore, all air samples, in which concentrations of relevant gases were beyond the limit of two standard deviations, calculated from the mean value (in plus and in minus), were rejected. Table 2 presents descriptive statistics prepared for the base sample devoided of outliers by applying the mentioned rule.

TABLE 2

Basic statistical sample – after removing outliers

Variable	Descriptive statistics						
	Valid N	Mean	Minimum	Maximum	Percentile 90	Standard deviation	Skewness
Ethylene [ppm]	32463	0.036	0.01	0.62	0.07	0.041	4.992
Propylene [ppm]	32463	0.033	0.01	0.31	0.07	0.034	3.051
Acetylene [ppm]	32463	0.007	0.001	0.223	0.014	0.015	6.934
Carbon monoxide [ppm]	32463	6.955	1	34	18	7.205	1.524
Oxygen [%]	32463	19.471	11.55	20.78	20.68	1.499	-2.022
Nitrogen [%]	32463	78.055	54.72	79.99	79.69	2.914	-3.335
Carbon dioxide [%]	32463	0.614	0.01	10.85	1.59	0.811	3.224
Methane [%]	32463	1.854	0.00	29.49	6.12	3.791	3.230
Hydrogen [ppm]	32463	5.371	0.2	130.0	10.2	11.160	5.878
Graham's ratio	32463	0.00071	0.00002	0.00255	0.00160	0.00058	1.044
Graham's ratio denominator	32463	1.214	0.20	5.70	2.69	1.068	1.744

The analysis of the results in Table 2 shows that after rejecting outliers, the number of elements in the sample decreased to 32463. This treatment significantly improved the skewness of almost all analysed gas concentrations and brought their distributions closer to the normal distribution.

The mean concentrations of the considered gases did not indicate a fire hazard. Additionally, at least 90% of cases did not show signs of increased intensity of the coal self-heating process [5,16,17].

The prepared statistical sample in the further part of the article is named the „base sample".

5. Initial comparative analysis of the base sample with the results of chromatographic analyses of air samples taken from the areas of the four considered longwalls

After preparing the base sample – containing the results of chemical analyses of air samples taken from mining areas that were not subjected to nitrogen inertisation, for which the fire hazard level was determined by Graham's ratio as a normal situation [12] – it was compared to the concentrations of gases contained in the air samples originating from the areas of considered longwalls I, II, III and IV, for which Graham's ratio presented the same fire hazard level. Therefore, only those cases that met the following conditions were selected from samples taken from the areas of these longwalls:

- the value of Graham's ratio calculated on the basis of gas concentrations contained in the analysed air samples had to be in the range of $0 < G \leq 0.0025$ – i.e., the fire hazard in the samples was classified by this indicator as a normal situation [12],
- the nitrogen concentration in selected samples had to be higher than or equal to 80% – in this way, samples taken while nitrogen inertisation was not carried out, were rejected.

Tables 3, 4, 5 and 6 present descriptive statistics created for the selected results of precise chromatographic analyses of air samples taken from the regions of the analysed longwalls. Below each table, there is a short comparison of concentrations of some gases emitted in the coal self-heating process with their equivalents forming the base sample (Table 2).

TABLE 3

Descriptive statistics of the results of chromatographic analyses of air samples taken from the area of the longwall I – representing the normal situation according to Graham's ratio

Variable	Descriptive statistics (longwall I)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	14	2.499	0.37	8.38	0.38	4.99	2.171
Propylene [ppm]	14	2.458	0.50	10.47	0.57	6.44	2.775
Acetylene [ppm]	14	0.0065	0.001	0.032	0.003	0.014	0.008
Carbon monoxide [ppm]	14	79.214	3	430	3	172	116.078
Oxygen [%]	14	5.683	3.47	8.27	3.49	7.74	1.698
Nitrogen [%]	14	93.588	91.37	95.96	91.43	95.58	1.585
Carbon dioxide [%]	14	0.634	0.21	1.52	0.29	0.95	0.348
Methane [%]	14	0.014	0.00	0.05	0.00	0.05	0.023
Hydrogen [ppm]	14	17.221	3.4	131.0	4.1	29.4	33.539
Graham's ratio	14	0.00040	0.00002	0.00199	0.00002	0.00102	0.00055
Graham's ratio denominator	14	19.118	15.96	21.94	16.47	21.733	2.105

While analysing the data contained in Table 3, it can be concluded that the mean concentrations of some gases emitted in the coal self-heating process (ethylene, propylene, carbon monoxide and hydrogen) contained in the air samples selected from the area of longwall I exceeded the average concentrations of their equivalents from Table 2 (in the case of ethylene and propylene even by up to two orders). Although, the average Graham's ratio value was lower than in the base sample. In addition, the mean concentrations of ethylene, propylene and carbon monoxide were even higher than the maximum concentrations of their equivalents from Table 2.

As for Graham's ratio denominator, its values in all samples exceeded the limit level of 5.7, which according to Słowik and Świerczek [14], allows to consider that Graham's ratio was beyond the scope of reliability and should not be taken into account when determining the level of fire hazard.

The average nitrogen concentration in the above air samples was 95.59%, which significantly exceeded the value of its equivalent from the base sample (78.06%).

TABLE 4

Descriptive statistics of the chromatographic analyses results of air samples taken from the area of longwall II – representing the normal situation according to Graham's ratio

Variable	Descriptive statistics (longwall II)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	202	3.817	0.10	12.70	0.95	8.97	3.073
Propylene [ppm]	202	3.233	0.18	13.75	0.66	5.60	2.321
Acetylene [ppm]	202	0.016	0.001	0.126	0.001	0.041	0.021
Carbon monoxide [ppm]	202	126.337	2	565	9	320	129.306
Oxygen [%]	202	4.851	0.76	19.71	1.81	8.63	3.439
Nitrogen [%]	202	93.260	80.01	97.83	89.40	96.50	3.331
Carbon dioxide [%]	202	1.735	0.07	5.79	1.16	2.24	0.678
Methane [%]	202	0.098	0.00	2.32	0.05	0.15	0.170
Hydrogen [ppm]	202	50.116	0.7	750.0	5.1	116.0	85.337
Graham's ratio	202	0.00066	0.00001	0.00252	0.00004	0.00168	0.00063
Graham's ratio denominator	202	19.863	1.49	25.09	15.06	23.689	4.308

The analysis of the data presented in Table 4 shows that the mean concentrations of ethylene, propylene, acetylene, carbon monoxide and hydrogen contained in the air samples selected from the area of longwall II exceeded the mean concentrations of these gases determined for samples taken from regions which were not subjected to nitrogen inertisation (Table 2) – although Graham's ratio classified both groups as a normal situation [12]. The mean concentrations of ethylene, propylene and carbon monoxide exceeded the average concentrations of their equivalents from the base sample by two orders. Based on the percentile 10, it can also be asserted that at least 90% of ethylene and propylene concentrations exceeded the maximum concentrations of these gases described in Table 2.

It was also observed that in at least 90% of air samples Graham's ratio denominator value significantly exceeded the limit level of 5.7, which does not allow to correctly classify the level of fire hazard based on this ratio [14].

The mean nitrogen concentration in these air samples was 93.26%, which significantly exceeded the value of its equivalent from the base sample (78.06%).

The analysis of the data contained in Table 5 shows that the mean concentrations of gases that are emitted in the coal self-heating process – contained in air samples selected from the area

TABLE 5

Descriptive statistics of the chromatographic analyses results of air samples taken from the area of longwall III – representing the normal situation according to Graham's ratio

Variable	Descriptive statistics (longwall III)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	830	0.180	0.01	4.39	0.03	0.28	0.319
Propylene [ppm]	830	0.204	0.01	4.84	0.02	0.34	0.511
Acetylene [ppm]	830	0.015	0.001	0.642	0.001	0.028	0.036
Carbon monoxide [ppm]	830	27.802	1	417	1	74	37.913
Oxygen [%]	830	13.619	0.65	19.79	2.61	19.07	5.811
Nitrogen [%]	830	84.453	80.01	99.24	80.30	94.10	5.219
Carbon dioxide [%]	830	1.112	0.05	6.72	0.05	2.88	1.100
Methane [%]	830	0.811	0.00	11.98	0.00	2.88	1.942
Hydrogen [ppm]	830	21.379	0.5	610.0	1.0	36.4	67.479
Graham's ratio	830	0.00052	0.00000	0.00253	0.00001	0.00140	0.00058
Graham's ratio denominator	830	8.761	1.43	25.62	2.24	21.367	7.067

of longwall III – did not reach such high levels as in the first and second longwall. The above can prove the fact that the fire hazard in the goaf of the longwall III was lower than in the two previous cases. However, also in this longwall, it was noticed that the mean concentrations of ethylene, propylene, acetylene, carbon monoxide and hydrogen exceeded the mean concentrations of their equivalents from the base sample by one order – even though Graham's ratio assigned both compared groups to the normal situation [12] (i.e. in which there is no fire hazard).

TABLE 6

Descriptive statistics of the chromatographic analyses results of air samples taken from the area of longwall IV – representing the normal situation according to Graham's ratio

Variable	Descriptive statistics (longwall IV)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	85	0.655	0.04	6.87	0.11	0.96	1.058
Propylene [ppm]	85	0.187	0.04	0.87	0.06	0.31	0.132
Acetylene [ppm]	85	0.006	0.001	0.102	0.001	0.013	0.015
Carbon monoxide [ppm]	85	63.800	1	270	7	120	55.514
Oxygen [%]	85	7.055	0.63	17.04	1.27	15.47	5.673
Nitrogen [%]	85	86.694	80.14	95.65	81.35	94.11	4.888
Carbon dioxide [%]	85	1.132	0.17	4.20	0.42	1.72	0.812
Methane [%]	85	4.998	0.33	14.74	0.71	11.97	4.366
Hydrogen [ppm]	85	32.769	5.8	112.0	7.9	65.9	25.797
Graham's ratio	85	0.00054	0.00001	0.00234	0.00004	0.00142	0.00057
Graham's ratio denominator	85	15.919	4.81	23.33	5.90	22.556	6.582

Additionally, it was found that the mean value of Graham's ratio was lower than its equivalent from the base sample.

Also, in this case, the average nitrogen concentration exceeded the value of its equivalent from the base sample (78.06%) and it was 84.45%.

In the case of samples selected from the area of longwall IV, the mean concentrations of ethylene, propylene, carbon monoxide and hydrogen exceeded by one order the mean concentrations of their equivalents from table 2. In addition, it was found that the mean concentrations of ethylene and carbon monoxide exceeded even the maximum concentration of these gases contained in the base sample which, according to Graham's ratio, correspond to the same fire risk level.

Taking into account Graham's ratio denominator value (determined by the percentile 10), it can be concluded that at least 90% of cases exceeded the value of 5.7, which corresponds to the unreliable values of this ratio [14].

The mean nitrogen concentration in these air samples was 86.69% and exceeded the value of its equivalent from the base sample (78.06%).

In summarising the preliminary analysis of the influence of nitrogen inertisation on Graham's ratio value, one can state the following.

1. Even though selected air samples – taken from nitrogen inerted areas of longwalls I, II, III and IV – were classified by Graham's ratio as cases indicating no endogenous fire hazard [12], the mean concentrations of gases contained in them, emitted in the coal self-heating process, exceeded (and sometimes considerably) the mean concentrations of their equivalents from the base sample, which represented air samples included in the same hazard category but taken from areas which were not subjected to nitrogen inertisation.
2. The high value of Graham's ratio denominator (causing the decrease of the real fire hazard level by this indicator) was the result of the high nitrogen concentration in the analysed air samples. This was probably due to the fact that only a small amount of this inert gas flowed through the self-heating coal centre before it reached the place for taking gas samples for testing.

6. Verification of the upper limit of the Graham's ratio reliability range on the air samples taken from the areas of the longwalls subjected to nitrogen inertisation

Based on the analyses carried out, the following question should be asked: when – during the nitrogen inertisation of mining areas – can it be claimed with a high degree of certainty that Graham's ratio values determined for air samples taken from those regions represent the actual fire hazard level?

The starting point may be the conclusions presented by Słowik and Świerczek [14], who on the example of the 2777-element statistical sample determined the upper limit of reliability of the Graham's ratio. According to them, if Graham's ratio denominator is higher than or equal to 5.7, it can be concluded, at a probability level of 95%, that Graham's ratio generates unreliable values – it understates the actual level of fire hazard.

Based on this statement, from air samples taken from the areas of considered longwalls I, II, III and IV – for which the fire hazard level was determined by Graham's ratio as a normal situation [12] and which contained a nitrogen concentration higher than or equal to 80% – cases, for which Graham's ratio denominator exceeded the value of 5.7, were rejected. Tables 7, 8 and 9 contain descriptive statistics prepared for the results of chromatographic analyses of air samples that were not rejected according to the mentioned condition, i.e. which according to Graham's ratio were at 95% probability level correctly classified as not indicating the existence of endogenous fire hazard [14].

TABLE 7

Descriptive statistics of the results of chromatographic analyses of air samples taken from the area of the longwall II – cases for which the Graham's ratio denominator < 5.7

Variable	Descriptive statistics (longwall II)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	5	0.770	0.17	1.62	0.17	1.62	0.694
Propylene [ppm]	5	1.168	0.18	2.80	0.18	2.80	1.074
Acetylene [ppm]	5	0.003	0.001	0.005	0.001	0.005	0.002
Carbon monoxide [ppm]	5	25.600	7	46	7	46	17.213
Oxygen [%]	5	18.416	16.79	19.71	16.79	19.71	1.112
Nitrogen [%]	5	81.042	80.01	82.50	80.01	82.50	0.996
Carbon dioxide [%]	5	0.474	0.20	0.71	0.20	0.71	0.241
Methane [%]	5	0.068	0.05	0.11	0.05	0.11	0.024
Hydrogen [ppm]	5	27.360	4.5	84.2	4.5	84.2	32.425
Graham's ratio	5	0.00090	0.00029	0.00213	0.00029	0.00213	0.001
Graham's ratio denominator	5	3.060	1.49	5.07	1.49	5.073	1.371

TABLE 8

Descriptive statistics of the results of chromatographic analyses of air samples taken from the area of the longwall III – cases for which the Graham's ratio denominator < 5.7

Variable	Descriptive statistics (longwall III)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	396	0.095	0.01	1.21	0.04	0.15	0.077
Propylene [ppm]	396	0.056	0.01	0.68	0.02	0.10	0.060
Acetylene [ppm]	396	0.019	0.001	0.242	0.002	0.041	0.029
Carbon monoxide [ppm]	396	23.326	1	130	4	53	22.254
Oxygen [%]	396	18.064	15.91	19.79	16.67	19.34	1.011
Nitrogen [%]	396	81.094	80.01	82.96	80.17	82.21	0.768
Carbon dioxide [%]	396	0.681	0.05	2.65	0.26	1.27	0.418
Methane [%]	396	0.159	0.00	2.87	0.00	0.62	0.430
Hydrogen [ppm]	396	5.851	0.5	480.0	0.8	7.1	26.389
Graham's ratio	396	0.00069	0.00002	0.00253	0.00013	0.00151	0.00057
Graham's ratio denominator	396	3.425	1.43	5.70	1.92	5.079	1.184

TABLE 9

Descriptive statistics of the results of chromatographic analyses of air samples taken from the area of the longwall IV – cases for which the Graham's ratio denominator < 5.7

Variable	Descriptive statistics (longwall IV)						
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Standard deviation
Ethylene [ppm]	7	0.111	0.04	0.17	0.04	0.17	0.042
Propylene [ppm]	7	0.056	0.04	0.08	0.04	0.08	0.013
Acetylene [ppm]	7	0.002	0.001	0.002	0.001	0.002	0.000
Carbon monoxide [ppm]	7	74.429	11	120	11	120	32.536
Oxygen [%]	7	16.496	15.94	17.04	15.94	17.04	0.324
Nitrogen [%]	7	81.383	80.66	82.44	80.66	82.44	0.646
Carbon dioxide [%]	7	1.317	0.17	2.24	0.17	2.24	0.681
Methane [%]	7	0.763	0.33	1.75	0.33	1.75	0.468
Hydrogen [ppm]	7	9.943	7.3	18.5	7.3	18.5	3.868
Graham's ratio	7	0.00146	0.00023	0.00234	0.00023	0.00234	0.001
Graham's ratio denominator	7	5.071	4.81	5.54	4.81	5.54	0.265

After the rejection of the air samples for which Graham's ratio denominator value was higher than or equal to 5.7, the following is concluded.

1. The table with descriptive statistics for air samples taken from the area of the longwall I was not possible to prepare, because all samples (according to the given criterion) were rejected. This means that with a probability of 95% in all these cases, Graham's ratio was unreliable [14].
2. The number of air samples taken from the areas of other longwalls, which Graham's ratio (according to the given criterion) correctly classified as samples in which there is no threat of endogenous fire, developed as follows:
   - longwall II – 5 samples remained – i.e. 97.5% of 202 samples were rejected,
   - longwall III – 396 samples remained – i.e. 52.3% of 830 samples were rejected,
   - longwall IV – 7 samples remained – i.e. 91.8% of 85 samples were rejected.
3. Despite the application of discussed criterion, the mean concentrations of some gases emitted in the coal self-heating process (contained in the remaining 408 air samples taken from longwalls II, III and IV) still clearly exceeded the average concentrations of their equivalents from the base sample (Table 2) – for which the fire hazard level was determined by Graham's ratio as a normal situation [12], but in areas which were not subjected to nitrogen inertisation. It follows that the rejection of the cases in which Graham's ratio denominator exceeded the value of 5.7 was probably an insufficient reliability criterion of this ratio for air samples originating from longwall areas where nitrogen is used as an inert gas.

Based on the presented conclusions, the values of Graham's ratio and the concentrations of selected gases in the base sample and the remaining 408 air samples, collected from longwall II, III and IV, were compared. The results of the analysis are well reflected by the statistics presented in the box and whisker plots, which show the mean value, standard deviation (boxes) and the confidence interval (whiskers) – Figure 1.

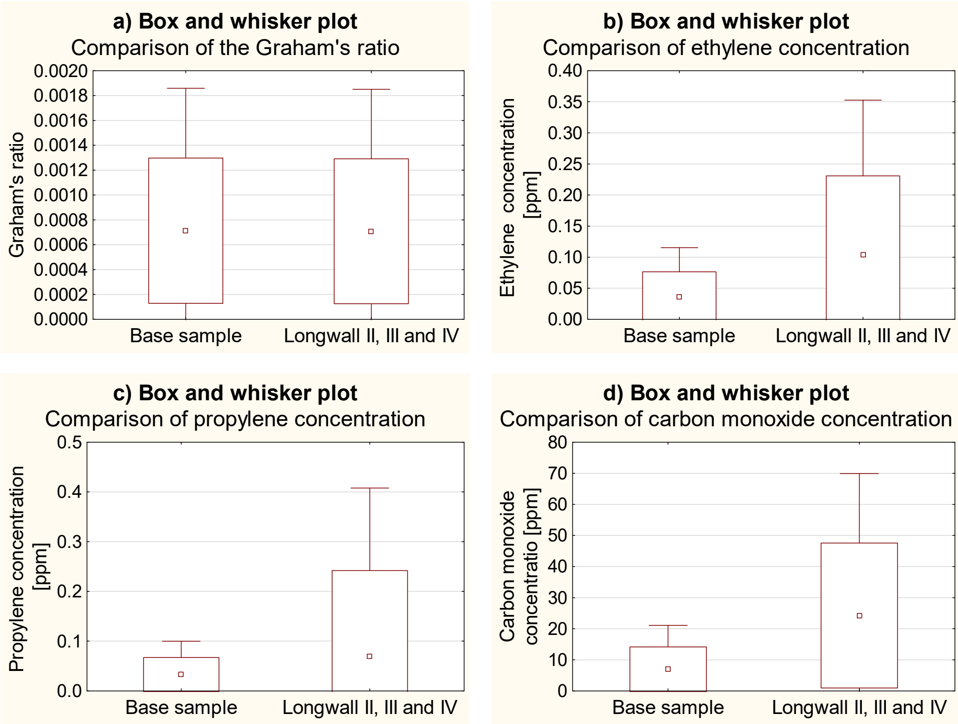

Fig. 1. Graphical interpretation of the comparison of the Graham's ratio values and concentrations of selected gases in the base sample and the remaining 408 air samples

The analysis of Figure 1 shows that when it comes to the values of Graham's ratio (Fig. 1a), both the mean and the dispersion of values almost match in both cases. However, taking into account the concentrations of selected gases released in the coal self-heating process (Fig. 1b, Fig. 1c and Fig. 1d), the average concentration for 408 air samples taken from the areas of longwalls II, III and IV were higher than in the base sample. The standard deviation of these 408 samples showed a greater scatter of values around the mean than in the base sample. The above proves that in the 408-element sample there were cases where the fire hazard was at a higher level than indicated by Graham's ratio condition.

Therefore, it can be concluded that it would be necessary to develop an additional criterion that would allow determining the state of fire hazard for cases that, according to the reliable value of Graham's ratio, were classified as not endangered, but there is a reasonable suspicion that we are dealing with an increased level of risk. This condition would be crucial in the case of air samples taken from areas of the longwalls where nitrogen is used as the inert gas.

7. Summary

This article presents a comparison of descriptive statistics prepared for the results of precise chromatographic analyses of air samples taken from the goafs of longwalls I, II, III and IV (where nitrogen was used as an inert gas) with results from samples taken in areas where no inertisation using this gas was applied. During the comparative analysis, only those cases were considered, for which the level of fire hazard was determined, as a normal situation by Graham's ratio [12].

A comparative analysis showed that the average concentrations of some gases emitted in the coal self-heating process (such as ethylene, propylene, acetylene, carbon monoxide and hydrogen) contained in the samples taken from the areas subjected to nitrogen inertisation, significantly exceeded the average concentrations of their equivalents from the samples originating from places where nitrogen was not used as an inert gas. It means that the air samples taken from the goafs of the longwalls where the nitrogen inertisation was carried out probably represented a higher level of fire hazard than it was due to the determined Graham's ratio values.

Undoubtedly, the understated values of Graham's ratio are due to the mathematical construction of the formula, based on which it is determined, because nitrogen is included in its denominator. Therefore, any increased concentration of this gas may cause the overstatement of Graham's ratio denominator, which may result in lower levels of risk presented by this indicator. This issue was described, among others, by Słowik and Świerczek [14] who, at the probability level of 95%, gave Graham's ratio reliability interval. According to their theory, if the value of Graham's ratio denominator is greater than or equal to 5.7, its indications are unreliable – it understate the real level of endogenous fire hazard.

However, after rejecting from the set containing the results of chromatographic analyses of air samples, taken from nitrogen inerted areas of longwalls I, II, III and IV, those cases for which Graham's ratio value (according to the given criterion) was unreliable, mean concentrations of significant gases still were higher therein than in samples originating from areas which were not subjected to nitrogen inertisation. This indicates the probably higher level of fire hazard represented by these samples than the normal situation presented by Graham's ratio.

Therefore, the conducted analyses showed that Graham's ratio reliability criterion [14] may not be sufficient for air samples originating from mining areas subjected to nitrogen inertisation. That is why the problem of unreliable values of Graham's ratio determined on the basis of air samples taken from areas where nitrogen is used as an inert gas will be further analysed.

Funding

This research was funded by the Ministry of Science and Higher Education, Poland, grant number: 11132049.

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