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S. A. EPSHTEIN[1], *Head of Laboratory, Doctor of Engineering Sciences, apshtein@yandex.ru*
E. E. SOKOLOVSKAYA[1], *Leading Engineer*
N. N. DOBRYAKOVA[1], *Researcher, Candidate of Engineering Sciences*
HAO J.[1], *Engineer, Associate Professor*

[1] *National University of Science and Technology MISiS, Moscow, Russian Federation*

DEVELOPMENT OF POTENTIOMETRIC TITRATION METHOD FOR ASSESSING COALS' OXIDATION DEGREE*

Oxidation of coal leads to some unwanted consequences, such as losses of products quality and increase in proneness to spontaneous combustion. One of the indicators of coals' oxidation is changing in amount and composition of active functional groups in organic matter. On using a wide number of samples and adjusting the experimental procedure, a method was developed for coals' oxidation degree evaluation by potentiometric titration based on evaluation of contents of total acidic groups (a sum of phenol and carboxyl groups). It was shown that potentiometric titration is not applicable for determination of phenol and carboxyl groups in coals separately. A phenomenon of appearance of two waves at titration curve was connected with absorption of CO_2 from air into the alcohol-alkaline solution. For coals with vitrinite reflectance varying in range of 0.5-0.72 %., total acidic groups amount decrease with rank growth, whereas for higher rank coals such an alteration is less pronounced. It is shown that it is expedient to use the developed method of potentiometric titration together with the petrographic method for determining the oxidation degree. On the basis of the proposed method of coals' oxidation degree determination by potentiometric titration, a National standard of the Russian Federation GOST R 59012-2020 has been introduced. According to it, the oxidation degree is determined by the increase of the total amount of acidic groups – phenolic and carboxyl hydroxyls in coal as compared to the content of total acidic groups in the control sample, which is used as a seam sample of coal taken outside the oxidation zone, or coal taken when laying the pile, or coal received for benefication, sorting or moving.

Keywords: *coal; oxidation degree; active functional groups; phenol groups, carboxyl groups, ion-exchange analysis, potentiometric titration, quantification*
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Introduction

Coal oxidation is a process leading to decrease of products quality and reasons for self-heating and, consequently, to spontaneous combustion [1, 2]. This occurs even at the initial stages of oxidation and the latter leads to substantial descend of coal products quality [3]. Oxidation processes also lead to alteration of quantity and composition of active functional groups in coal matter – phenol, carboxyl, carbonyl and quinoid ones [2].

Presence of active groups within coals depends, primarily, on coal nature, including oxygen occurrence and its forms. Phenol and carboxyl active groups are sometimes being united into total acidic groups (TA) and are referred to coal chemical activity during sorption and chemisorption [4]. It is well known that TA groups are present in unoxidized coals, with their amount descending with coal rank [5]. As for the oxidized coals, their number is higher as compared with unoxidized ones [6]. Carboxyl groups appear in hard coals only under oxidation processes due to formation of humic acids [7].

Therefore, it is obvious that quantitative determination of active groups in coals is a way of characterization of their oxidation degree. Currently there exist various methods of investigation of oxygen-containing functional groups in coals. Such methods could be divided into two major groups, namely, physical (instrumental), and chemical ones.

The most widespread technique for determination of oxygen-containing functional groups in coals is Fourier-transform infrared spectra analysis (FTIR). Results of such analyses allowed establishing changes in coals' oxidation propensity with rank by considering the functional groups [8]. But again, it should be noted that FTIR methods allow, primarily, a qualitative analysis of oxygen and oxygen-containing functional groups [9], whereas for quantification of such data it is mandatory to combine them with other techniques, such as chemical analyses [10].

The solid-state analysis of functional groups at coals surfaces (when using a grinded coal samples) is usually performed by proton nuclear magnetic resonance spectroscopy measurements (NMR). The specific features of such measurements is that NMR allows a direct measurement of shares of the functional groups by the rise of corresponding bands [11]. Nevertheless, despite to the fact that NMR methods give an opportunity to characterize coals organic matter structure, a more detailed analysis is needed to quantify these measurements, especially in the view of oxygen functional groups contents evaluation and characterization [12].

The main method of chemical analysis and quantification of functional groups in coal structure is ion exchange analysis. This technique is based on titration and is rather easy to be implemented in practice. Usually the titration is based on two separate approaches, namely, colorimetric [13] and potentiometric [14, 15]. Indirectly, a method regulated by ASTM D5263-2015 [16] could also be referred to titration, but without quantification of functional groups.

The essence of colorimetric titration lies in identification of the endpoint by change in colour of the reactant indicator [17] or by newest methods of colorimetry, namely, instrumental techniques [13]. In most cases, colorimetric analysis of functional groups in coals becomes challenging due to initially highly coloured solutions of coals extracts. The limitations of such method made it to cancel a standard method of coals' oxidation degree determination by evaluation of total contents of phenol and carboxyl active groups by colorimetric titration. In the view of above, the potentiometric titration became a more promising method for coal functional groups analysis [18].

Potentiometric titration is used for both total acidic functional groups quantification [15], and carboxyl ones separately [19], whereas phenol groups are usually found by difference [20]. To this end, different solvents (aqueous [21] and non-aqueous [22]) are used by different authors. Some researchers report on indication of different types of oxygen-containing functional groups by different inclination angles and

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inflections at titration curves obtained in aqueous solution [23, 24]. Nonetheless, in most cases, the aims of the studies are to find a total amount of acidic groups in coal matter. In general, due to the solvation methods of the coal organic matter, the analysed functional groups are primarily located at the coals surface, whereas the internal ones, that are hard to be extracted, are left to remain. Therefore, ion exchange analysis methods allow characterization of total sorption activity of humic acids [24], whereas for coals, these results are not usually applicable for characterization of entire possible activity, but only the surface sorption properties and, consequently, coals' oxidation degree [21, 23].

In this paper, the results were presented on evaluation of amount of acidic functional groups in hard coals of different rank with help of potentiometric titration. The aim of the work was to update the conditions for preparing and conducting of the potentiometric titration procedure, as well as the results interpretation.

Materials and Methods

1. Samples characterization and preparation

A large collection of coals was used containing hard coals of different rank and anthracite. Samples preparation and characterization was performed according to the standard techniques. Petrographic, proximate and ultimate analyses were also performed by standard methods applicable to all the considered coals. Vitrinite reflectance index $R_{o,r}$ was measured in accordance with ISO 7404-5:2009, analytical moisture W^a by ISO 11722:2013, ISO 5068-2:2007, ash A^d (on dry basis) with ISO 1171:2010, volatile matter V^{daf} (on dry, ash-free basis) by ISO 562:2010, gross calorific value Q_s^{daf} (on dry, ash-free basis) was found using ISO 1928:2009. Elemental analysis (ultimate analysis) was done in accordance with ISO 17247:2005, Sulphur S_t^d (on dry basis) contents were found in accordance with ISO 19579:2006.

Table 1. Characteristics of samples

Sample #	Origin	V_t, %	R_{or}, %	Proximate analysis, % mass				Q^{daf}, kJ/kg	Ultimate analysis, % mass (on dry, ash free basis)				Atomic H/C ratio, at	Atomic O/C ratio, at
				W^a	A^d	V^{daf}	S_t^d		C	H	N	O*		
1	Kuznetsk basin	55.00	1.04	1.24	11.30	21.90	0.16	33762.10	85.62	4.05	2.17	6.99	0.57	0.06
2	Kuznetsk basin	73.00	1.80	1.19	19.60	13.40	0.51	35022.92	88.56	3.91	2.23	3.70	0.53	0.03
3	Kuznetsk basin	63.00	0.96	1.01	18.90	23.70	0.33	34623.20	85.60	4.68	2.51	5.46	0.66	0.05
4	Kuznetsk basin	70.00	0.65	2.10	17.50	37.60	0.51	33329.36	79.84	4.56	2.24	9.37	0.69	0.09
5	Kuznetsk basin	65.00	0.50	3.15	15.30	38.80	0.37	31659.16	76.83	5.18	2.24	12.56	0.81	0.12
6	Kuznetsk basin	63.00	0.66	2.34	13.10	35.70	0.41	33142.00	81.14	5.17	2.26	9.31	0.77	0.09
7	Donetsk basin	91.00	3.58	1.18	4.30	3.50	2.48	36684.53	92.39	1.62	1.15	2.13	0.21	0.02
8	Irkutsk basin	96.00	0.51	4.85	23.10	45.90	1.01	32067.29	75.74	5.77	1.60	11.40	0.91	0.11
9	Ulug-Khemsky basin	88.00	0.72	0.56	6.16	39.10	0.44	35554.31	88.28	6.17	1.55	3.39	0.84	0.03
10	Ulug-Khemsky basin	95.00	0.53	1.57	4.35	45.60	0.28	33938.20	84.28	6.00	1.29	7.76	0.85	0.07
11	Ulug-Khemsky basin	94.00	0.56	1.60	5.71	44.00	0.42	34134.98	83.19	5.94	1.29	7.30	0.86	0.07
12	Apsatsky deposit	94.73	1.05	0.46	14.16	26.12	0.41	34591.34	90.00	5.07	1.09	2.87	0.68	0.02
13	Apsatsky deposit	87.77	1.07	0.73	10.74	25.49	0.34	35663.16	89.38	5.05	0.95	3.75	0.68	0.03
14	Apsatsky deposit	87.34	1.18	0.61	16.31	23.57	0.31	35654.79	91.07	4.88	0.96	2.26	0.64	0.02
15	Apsatsky deposit	91.82	1.11	0.64	9.76	22.85	0.26	35801.33	90.45	4.87	1.02	3.02	0.65	0.03
16	Apsatsky deposit	89.60	1.10	0.47	8.77	23.62	0.25	36395.85	91.08	5.06	0.83	2.50	0.67	0.02
17	Apsatsky deposit	86.30	1.09	0.94	12.66	23.28	0.23	35056.08	89.46	4.72	0.87	4.05	0.63	0.03
18	Apsatsky deposit	87.60	1.07	0.79	9.79	25.50	0.29	35646.42	89.89	5.02	1.02	3.36	0.67	0.03
19	Olon-Shibir deposit	93.06	0.50	2.65	32.73	47.22	0.57	30605.51	76.97	5.88	1.21	9.89	0.92	0.10
20	Olon-Shibir deposit	84.54	0.50	2.65	32.02	45.01	0.47	30869.28	77.59	5.79	1.04	9.85	0.90	0.10
21	Olon-Shibir deposit	88.11	0.50	3.28	10.43	45.47	0.31	32435.14	80.28	5.86	1.21	10.76	0.88	0.10
22	Nikolskoe deposit	86.79	0.50	2.32	19.32	44.31	0.38	32853.82	81.59	5.88	1.26	8.51	0.87	0.08
23	Nikolskoe deposit	85.60	0.56	2.02	12.80	43.30	0.39	32389.08	79.10	5.34	1.03	12.03	0.81	0.11
24	Kuznetsk basin (naturally oxidized)	82.00	0.43	6.84	14.80	41.60	0.42	28137.26	67.24	5.03	2.27	19.81	0.90	0.22
25	Kuznetsk basin (naturally oxidized)	70.00	1.52	1.77	26.40	18.70	0.65	33896.12	86.16	4.10	2.31	4.74	0.57	0.04
26	Nikolskoe deposit (naturally oxidized)	89.70	0.52	6.83	21.40	44.50	0.66	28516.29	74.90	4.50	1.36	13.49	0.72	0.14
27	Nikolskoe deposit (naturally oxidized)	89.20	0.55	13.02	20.40	46.70	0.24	23374.90	67.00	3.32	1.46	19.33	0.59	0.22

Notations: V_t – Vitrinite content (on mineral matter free basis); $R_{o,r}$ – Vitrinite reflectance index; W^a – Moisture; A^d – Ash (on dry basis); V^{daf} – Volatile matter (on dry, ash free basis); S_t^d – Total Sulphur (on dry basis); Q^{daf}, kJ/kg – Calorific value (on dry, ash-free basis); *O calculated by difference

Table 1 contains all the obtained quality indices of the considered samples, along with their origin.

It could be seen from Table 1 that the considered hard coals differ from subbituminous (samples ## 5, 8, 10, 11, 19–23) to bituminous ones (samples ## 1–4, 6, 9, 12–17) and anthracite (#7). They also vary by origin and quality indices, such as calorific value and Carbon contents. Anthracite sample that was included in the collection is characterized by the highest Carbon contents, lowest H/C ratio (i.e. the highest aromaticity degree [25, 26]) and relatively high value of Sulphur. Four naturally oxidized coals were also added to the sample set, namely, ##24–27. They are characterized by lower calorific value and carbon contents with higher oxygen contents as compared to coals of the same origin but unoxidized (see, e.g. coals ##2 and 25, and ##6 and 24). It also should be mentioned that coals 23, 26 and 27 are of the same origin, but with different oxidation degree, with #23 an unoxidized one.

2. Potentiometric titration apparatus and samples preparation

All samples from the collection were conditioned to air-dry state, grinded to the particles size of <200 μm. Afterwards, they were stored in containers under conditions excluding their oxidation prior to the main experimental procedures.

In order to evaluate the contents of total carboxyl and phenol groups in coals samples, and ion exchange analysis was used by potentiometric titration was used as it will be described in the "Results and discussion" (1) section. Titration process was implemented using precision automatic titrator 'Titrion' along with liquid analyzer 'Expert-001'. Results of potentiometric titration are found and processed by 'Titrion' software.

In order to develop the potentiometric titration method for evaluation of TA groups in coals, a wide set of preliminary experiments was conducted aimed at adjustment of solution, time of titration, interpretation of titration curves shapes, etc. On its basis, the optimal conditions for preparing and conducting the experiments, and their results interpretation. In "Results and discussion" (1) section, only the final procedure with optimal conditions is being shown.

3. Method for evaluation of carboxyl groups by ion exchange analysis and further determination of amount of phenol groups

Carboxyl groups (CBS) were evaluated separately. The essence of the further described method is the interaction of CBS groups with the calcium acetate solution. This method was previously developed by [27] and is being widely used for evaluation of carboxyl groups in humic acids and coals [28, 29]. The following reaction is the basis of it (see eq. (1)), where the active carboxyl groups at the coals matter surface interact with the saline by formation of insoluble humates:

$$2R(COOH)m + m(CH_3COO)_2Ca \leftrightarrows 2R[(COO)_2Ca]m + 2mCH_3COOH \quad (1)$$

Hydrogen within the CBS groups is being replaced by the metal (saline formation). Therefore, carboxyl groups amount is equivalent to the difference between the volume of the released acid from the sample of coal and the volume of free acetic acid contained in the calcium acetate solution.

Coals samples of 0.0500 ± 0.0002 g are put into conical vessels (of 25 cm^3 volume) and 20 cm^3 of aqueous solution of 0.4N calcium acetate is added (main experiment). 20 cm^3 of 0.4N calcium acetate aqueous solution also is poured to the separate analogous vessel (reference experiment). The normality of the acetic acid present in the calcium acetate solution is determined at the same day.

The prepared solutions are being stored in a dark place at ambient temperature for 72 h with periodic mixing. During mixing, it is mandatory not to allow the coals samples to reach the vessel walls and cover.

After 72 hours of solutions storage, the last mixing is being performed. After, the solution allows to stand until complete sedimentation of the sample particles to the bottom of the vessel. The latter allows to proceed with titration.

Titration procedure consists of the following. Conical vessel of 100 cm^3 volume is filled with 10–15 cm^3 of deionized water. 10 cm^3 of calcium acetate solution selected by the pipette over the settled coal sample is added, as well as five to six droplets of indicator. The obtained solution is titrated with NaOH until weak pink and lilac coloring appears. The reference sample that was stored at the same conditions is titrated according to the similar procedure.

Normality of acetic acid in the solution of the main experiment and reference sample (N_{CH_3COOH}) is found according to eq. (2):

$$N_{CH_3COOH} = N_{NaOH}V_{NaOH}/V_{(CH_3COOH)_2Ca}, \quad (2)$$

where N_{NaOH} is the normality of NaOH solution, V_{NaOH} is the volume of NaOH used for titration of calcium acetate aliquote (cm^3), $V_{(CH_3COOH)_2Ca}$ is the volume of calcium acetate solution taken for titration (10 cm^3).

Amount of carboxyl groups (M_2) could be calculated in accordance with two equivalent formulae (see eq. 3 and 4).

$$M_2 = (2V^P_{NaOH}N_{NaOH} - 20N_{CH_3COOH})/m, \quad (3)$$

$$M_2 = 1000(V^P_{NaOH} - V^k_{NaOH})N_{NaOH}V_{(CH_3COOH)_2Ca}/(1000V_{al}m), \quad (4)$$

where V^P_{NaOH} is the volume of NaOH solution taken for titration of the aliquote of calcium acetate solution with coal sample (cm^3), V^k_{NaOH} is the volume of NaOH solution taken for titration of the aliquote of calcium acetate solution without coal sample (reference experiment) (cm^3), N_{CH_3COOH} is the normality of the acetic acid within the calcium acetate solution of the reference experiment (determined at the day of the titration), V_{al} is the volume of calcium acetate solution used for the coal sample treatment (20 cm^3), m is the mass of the coal sample used for the experiment (on dry, ash-free basis) (g).

Amount of phenol groups (PG) was evaluated for each of the coals by the difference between TA and CBS groups, as it was suggested in, e.g. [20] and many other works.

4. Determination of coals' oxidation degree by standard method

The degree of oxidation was determined by the standard (in the Russian Federation) method GOST 8930-2015 [30] using optical analysis. It is based on a petrographic approach of evaluation of coals oxidation by counting the grains' regions with and without indices of weathering. The essence of the method is to study (under a microscope in reflected light) a polished coal briquette in an immersion medium and to quantify, by microfeatures, the ratio Oks of weathered grains' areas to the total number of grain areas that fell into the field of view when counting by the point method (see eq. (5)). The oxidation indices obtained using this method are associated only with the occurrence of defects in the process of coal oxidation and do not reflect any changes in its chemical composition. The method is well tested, but has a low sensitivity, especially for coals at a low stage of oxidation.

$$Oks = B100/(B + H), \quad (5)$$

where, B is the number of oxidized grains, H is the number of non-weathered grains (zones) at the sample surface.

Results and discussion

1. Procedure for evaluation of total acidic groups by ion exchange analysis

In a conical vessel (Erlenmeyer flask), 6 g of KOH are dissimilated in 1000 cm^3 of C_2H_5OH and stored for 24 hrs. After, this solution is being decantated to another conical vessel. For the potentiometric titration, 1 g of solid grinded coal sample was inserted into Erlenmeyer flask with volume of 100 cm^3 and final alcohol solution of potassium hydroxide was added.

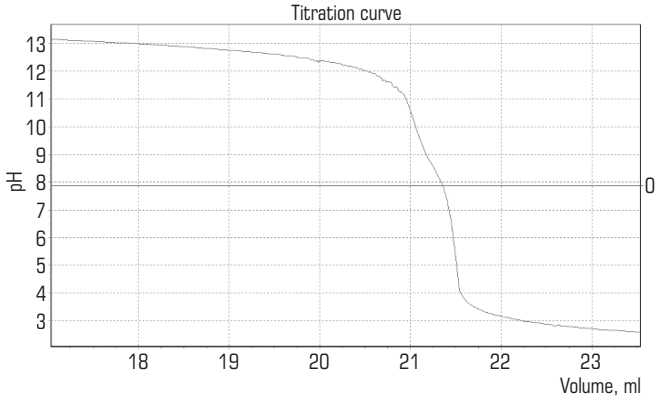

Fig. 1. Potentiometric curve at blank experiment (two different 'waves' are clearly seen)

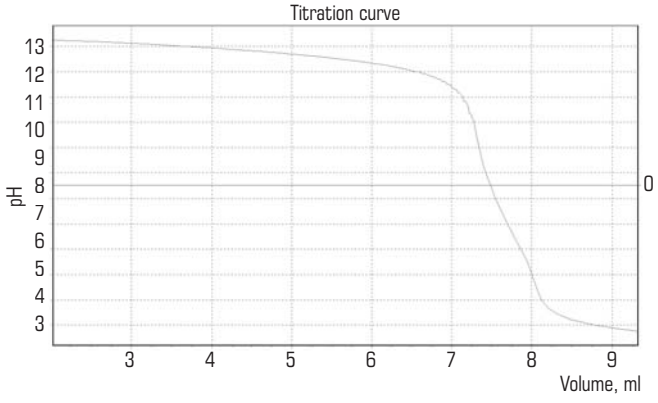

Fig. 2. Titration curve of the main experiment (coal #6) (two waves are observed at the exact same places as for blank analysis)

Table 2. TA, CBS and PG amounts evaluated at the selected coals

Sample #	On dry, ash-free basis		
	TA, mg-eq/g	CBS, mg-eq/g	PG, mg-eq/g
1	0.33	0.00	0.33
2	0.25	0.00	0.25
3	0.53	0.00	0.53
4	2.50	0.00	2.50
5	2.99	0.00	2.99
6	2.31	0.00	2.31
7	0.18	0.00	0.18
8	2.86	0.00	2.86
9	0.40	0.00	0.40
10	2.30	0.00	2.26
11	2.11	0.00	2.07
12	0.21	0.00	0.21
13	0.20	0.00	0.20
14	0.79	0.00	0.79
15	0.57	0.00	0.57
16	0.24	0.00	0.24
17	0.63	0.00	0.63
18	0.27	0.00	0.27
19	3.19	0.10	3.13
20	3.12	0.10	3.06
21	2.79	0.00	2.79
22	2.45	0.10	2.40
23	1.91	0.00	1.91
24 (naturally oxidized)	3.65	0.20	3.45
25 (naturally oxidized)	0.85	0.11	0.74
26 (naturally oxidized)	3.22	0.50	2.72
27 (naturally oxidized)	3.36	0.99	2.37

The flask was tightly closed and left for settling for 20 hours without additional shaking or mixing. After, the solution was filtered, the liquid sample of 25cm^3 was inserted to beaker of 50 cm^3 volume with magnetic stirring bar and electrode and placed to magnetic shaker of the titration equipment. For each coal, two samples were prepared by the aforementioned technique. For the blank titration, 0.1 N solution of alcohol and potassium hydroxide was used with volume of 25 cm^3. Titrant (0.1 N hydrochloric acid solution) was automatically supplied by the pump. The equivalency point is found as a potential jump during the alkali excess neutralization by hydrochloric acid. The volume of HCl solution that was consumed by alcohol-potassium hydroxide solution (without reaction with TA groups) was found according to the equipment readings. Further, amount of TA groups (mg-eq/g) is calculated using the following formula (6):

$$TA = (V - V_1)V_2 0.1/(V_3 m), \quad (6)$$

where V (cm^3) is the volume of 0.1 N HCl solution consumed by titration of the blank experiment, V_1 (cm^3) is the volume of 0.1 N HCl supplied for the main experiment of titration, V_2 (cm^3) is the volume of 0.1 N alcohol solution of KOH (50 cm^3), V_3 (cm^3) is the volume of 0.1 N filtrate of alcohol solution of KOH taken for titration (25 cm^3), m is mass of coal taken on dry, ash-free basis (g) as calculated by the following equality (7):

$$m = m_1(100 - W^a - A^a)/100, \quad (7)$$

where m_1 is the mass of coal sample taken for analysis (g), W^a is analytical moisture of coal (% mas), A^a is ash of coal (%).

The final result of TA groups evaluation is obtained as an average of two parallel measurements. Statistical processing of the results for the determination of TA groups in the range from 0.1 mg-eq/g to 3 and higher showed that the error of determination (repeatability limit) of the results does not exceed 5% (relative).

It should be especially pointed out that interpretation of the titration curves in these cases must be performed by consideration of blank experiment. As an example, we provide a typical blank experiment titration curve (see fig. 1). This curve was related to pre-analysis of coal #6 (oxidized low-rank one). It contains two 'waves' with different inclination angles. Some authors [23, 24] report on that these 'waves', when titrating the coal or humic acids, could be considered as signals from different active groups. On the other hand, here we report on such waves on the blank experiment. This could be explained by the fact that during the titration, the solution adsorbs some of CO_2 from the air (i.e. contains carbonates), thus giving the waves on the potentiometric curve.

Further experiment with coal revealed the similar waves were obtained (**fig. 2**), with their location at the same points. The location was found by mathematical processing of experimental data by finding the points referred to bending of the curve. In order to confirm the abovementioned supposition, we have calculated *TA* for the first and the second wave. The difference between these values was found to be within the error of measurement (not more than 5%). Thus, in our case we believe that it is wrong to interpret two waves as signals from different active groups and therefore we concentrated on finding only TA groups amount.

2. Functional groups in hard coals of different rank

Values of TA, CBS and PG amounts obtained at the coals sample set from table 1 are listed in **table 2**. It could be seen that oxidized coals have relatively higher amount of TA groups as compared to the unoxidized ones.

It could be seen in **fig. 3** and Table 2, that TA groups decay fast for coals with vitrinite reflectance range 0.50–0.72%, whereas in the range of 1.01–3.58%, the changes are not as pronounced. As it was expected, the lowest contents of TA groups was found for anthracite sample.

It should be especially pointed out that at most of the selected coals, carboxyl groups were not found which is in a good agreement with [7]. In oxidized coals ## 24–27, carboxyl groups appear, the amount of which varies from 0.11 to 0.99 mg-eq/g. Also, carboxyl groups were found for coals ## 19, 20 and 22.

3. Comparison between coals' oxidation degree by petrographic method and TA groups contents

Oxidation degree for selected coals #19, 20, 22, 24–27 (including naturally oxidized ones and those for which the carboxyl groups were found) was measured according to the petrographic technique described in section "Materials and methods" (3). The correlation between TA contents and parameter OKs (%) is shown in **Figure 4.**

Figure 4 shows that, in general, an increase in the oxidation degree of coal correlates with an increase in the number of TA groups. However, the relationship between TA and OKs parameters is not linear, deviations can be seen on the graph, apparently associated with differences in the sensitivity of the methods, especially at the low and high stages of coal oxidation. Therefore, it is advisable to use the developed method of potentiometric titration of alcohol-alkaline coals extracts in conjunction with the petrographic method for determining oxidation.

4. Standard method of coals' oxidation degree determination by potentiometric titration

On the basis of the current research, a national standard was developed (see GOST R 59012-2020 [31].

This Standard establishes a chemical method for determining the oxidation of coals by the total content of phenol and carboxyl groups in them using potentiometric titration. Oxidation degree is determined by the increase of the total amount of acidic groups – phenol and carboxyl hydroxyls in coal as compared to the content of total acidic groups in the control sample, which is used as a seam sample of coal taken outside the oxidation zone, or coal taken when laying the pile, or coal received for benefication, sorting or moving.

The precision of the method was determined based on a large number of tests. It depends on the TA groups amount as shown in **Table 3**.

The oxidation degree of coals is determined by comparing the data on the content of TA groups with the values obtained on control samples. The comparison is being carried out for values calculated on dry basis.

To assess the oxidation degree of coal during mining, the control sample may be selected as a seam sample of coal taken outside the oxidation zone.

To assess the change in coal oxidation during mining, a control sample can be a coal taken at various time stages of storage, starting from the laying of the stack.

To assess the change in oxidation at different technological stages, a control sample can be a sample of coal supplied for benefication, sorting and transportation.

To assess the oxidation degree, the difference between the content of total acidic groups in the tested coal sample and their content in the control sample is calculated and compared with the repeatability limit for the corresponding range of total acidic groups in coal. If the difference is less than the repeatability limit, then it is concluded that the increase in the oxidation of the test coal compared to the control sample did not occur. If the difference is more than the repeatability limit, then it is concluded that there has been an increase in the oxidation of coal compared to the control sample.

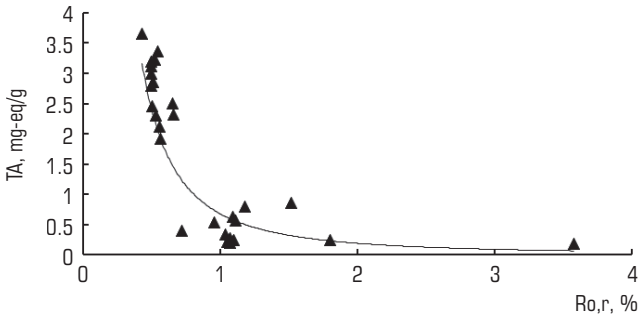

Fig. 3. Correlation between TA groups and coals rank

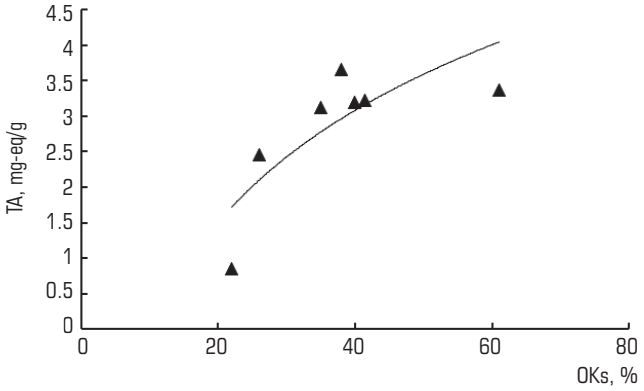

Fig. 4. Correlation between TA groups amounts in coals and their oxidation degree measured by petrographic technique

Table 3. Precision of the method

Range of TA groups (on dry basis), mg-eq/g	Precision (repeatability limit)
Less than (incl.) 1.00	0.05
1.00–3.00(incl.)	0.10
More than 3.00	0.15

Conclusions

It was demonstrated that the potentiometric titration of alcohol-alkali extracts of coals is not applicable for determination of phenol and carboxyl groups in coals separately. It was shown that two waves at titration curve appear due to the absorption of CO_2 from air into the solutions. Therefore, potentiometric titration technique is efficient only for determination of total acidic groups (a sum of phenol and carboxyl ones).

The changes of TA groups amount in coals with rank were discussed. It was shown that for coals with vitrinite reflectance varying in range of 0.5–0.72%, TA groups amount descend drastically with rank growth, whereas for coals with higher rank such an alteration is less pronounced.

It is shown that it is expedient to use the developed method of potentiometric titration together with the petrographic method for determining oxidation.

On the basis of the developed method of coals' oxidation degree determination by potentiometric titration, a National standard of the Russian Federation GOST R 59012-2020 has been developed and introduced. According to it, the oxidation degree is determined by the increase of the total amount of acidic groups – phenolic and carboxylic hydroxyls in coal as compared to the content of total acidic groups in the control sample, which is used as a seam sample of coal taken outside the oxidation zone, or coal taken when laying the pile, or coal received for benefication, sorting or moving.

References

1. Desna N. A., Miroshnichenko D. V. Oxidized coal in coking: A review. *Coke and Chemistry*. 2011. Vol. 54, No. 5. pp. 139–146.
2. Zhou C., Zhang Y., Wang J. et al. Study on the relationship between microscopic functional group and coal mass changes during low-temperature oxidation of coal. *International Journal of Coal Geology*. 2017. Vol. 171. pp. 212–222.
3. Beamish B. B., Barakat M. A., St. George J. D. Spontaneous-combustion propensity of New Zealand coals under adiabatic conditions. *International Journal of Coal Geology*. 2001. Vol. 45, No. 2–3. pp. 217–224.
4. Hao S., Wen J., Yu X., Chu W. Effect of the surface oxygen groups on methane adsorption on coals. *Applied Surface Science*. 2013. Vol. 264. pp. 433–442.
5. Chen Y., Mastalerz M., Schimmelmann A. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *International Journal of Coal Geology*. 2012. Vol. 104. pp. 22–33.
6. Semenova S. A., Patrakov Y. F., Majorov A. E. Assessment of the likelihood of underground coal oxidation and self-ignition: a review. *Coke and Chemistry*. 2020. Vol. 63, No. 5. pp. 223–231.
7. van Krevelen D. W. Coal: typology, physics, chemistry, constitution. Amsterdam ; New York : Elsevier, 1993. 1002 p.
8. He X., Liu X., Nie B., Song D. FTIR and Raman spectroscopy characterization of functional groups in various rank coals. *Fuel*. 2017. Vol. 206. pp. 555–563.
9. Semenova S. A., Patrakov Yu. F., Yarkova A. V. et al. Changes in the Properties of Native Low-Metamorphozed Coal in Contact with Air. *Khimiya tverdogo topliva*. 2022. No. 3. pp. 3–12.
10. Malysheva V. YU., Fedorova N. I., Ismagilov Z. R.. Study of brown coals by method of infrared spectroscopy. *Chemistry for sustainable development*. 2020. Vol. 28, No. 6. pp. 560–565.
11. Suggate R. P., Dickinson W. W. Carbon NMR of coals: the effects of coal type and rank. *International Journal of Coal Geology*. 2004. Vol. 57, Iss. 1. pp. 1–22.
12. Okolo G. N., Neomagus H. W. J. P., Everson R. C. et al. Chemical–structural properties of South African bituminous coals: Insights from wide angle XRD–carbon fraction analysis, ATR–FTIR, solid state 13 C NMR, and HRTEM techniques. *Fuel*. 2015. Vol. 158. pp. 779–792.
13. Kus J., Misz-Kennan M. Coal weathering and laboratory (artificial) coal oxidation. *International Journal of Coal Geology*. 2017. Vol. 171. pp. 12–36.
14. Yudina N. V., Savel'eva A. V., Linkevich E. V. Changes in the composition and properties of humic substances upon the mechanical treatment of coals with mineral salts. *Solid fuel chemistry*. 2021. Vol. 55, No. 4. pp. 229–235.
15. Khil'ko S. L., Rogatko M. I., Makarova R. A. Antiradical and potentiometric characteristics of humic substances from different natural sources. *Vestnik Donetsk National Technical University*. 2019. No. 1(15). pp. 73–79.
16. ASTM D5263-15 – Standard Test Method for Determining the Relative Degree of Oxidation in Bituminous Coal by Alkali Extraction. 2015. Available at: https://www.astm.org/d5263-15.html (accessed: 18.08.2022).
17. Marinov V. N. Self-ignition and mechanisms of interaction of coal with oxygen at low temperatures. 3. Changes in the composition of coal heated in air at 60 °C. *Fuel*. 1977. Vol. 56, Iss. 2. pp. 165–170.
18. Pringle W. J. S. Potentiometric Titration of Coal in a Non-Aqueous Medium. *Nature*. 1959. Vol. 183. pp. 815–816.
19. Murata S., Hosokawa M., Kidena K., Nomura M. Analysis of oxygen-functional groups in brown coals. *Fuel Processing Technology*. 2000. Vol. 67, Iss. 3. pp. 231–243.
20. Kolesnikova S. M., Kamenskii E. S., Kuznetsov P. N. et al. Activity of coals from mongolian deposits in the process of thermochemical degradation. *Solid Fuel Chemistry*. 2012. Vol. 46, No. 5. pp. 305–309.
21. Sakurovs R., Lewis C., Wibberley L. Effect of heat and moisture on surface titratability and pore size distribution of Victorian brown coals. *Fuel*. 2016. Vol. 172. pp. 124–129.
22. Clemow L. M., Jackson W. R. Non-aqueous titration of the acidic groups in coals: a warning! *Fuel*. 2002. Vol. 81, Iss. 7. pp. 959–961.
23. Saeed K., Ishaq M., Ahmad I., Shakirullah M., Park S. -Y. Investigation of surface acidity of coal by aqueous potentiometric titration. *Journal of chemical society of Pakistan*. 2007. Vol. 29, No. 2. pp. 111–115.
24. Khil'ko S. L., Kovtun A. I., Rybachenko V. I. Potentiometric titration of humic acids. *Solid Fuel Chemistry*. 2011. Vol. 45, No. 5. pp. 337–348.
25. Maroto-Valer M. M., Love G. D., Snape C. E. Relationship between carbon aromaticities and HC ratios for bituminous coals. *Fuel*. 1994. Vol. 73, Iss. 12. pp. 1926–1928.
26. Maroto-Valer M. M., Andrésen J. M., Snape C. E. Verification of the linear relationship between carbon aromaticities and H/C ratios for bituminous coals. *Fuel*. 1998. Vol. 77, Iss. 7. pp. 783–785.
27. Syskov K. I., Kukharenko T. A. Determination of constitutional groups in coals and their constituents by the sorption method. *Zavodskaya Laboratoriya*. 1947. Vol. 13, No. 1. pp. 25–28.
28. Golovin G. S., Lesnikova E. B., Artemova N. I., Dementeva O. A. Ion-exchange properties of lignites and products of their chemical modification. *Solid Fuel Chemistry*. 1996. Vol. 30, No. 5. pp. 24–28.
29. Golovin G. S., Lesnikova E. B., Artemova N. I., Lukicheva V. P. Ion-exchange properties of cation exchangers produced on the basis of brown coal from the Kansk-Achinsk basin. *Solid Fuel Chemistry*. 2000. Vol. 34, No. 4. pp. 32–38.
30. GOST 8930-2015 Hard coals. Method for determination of oxidation. Introduced: 2017–04–01. Moscow : Standartinform, 2017.
31. GOST R 59012-2020 Hard coals. Determination of oxidation by potentiometric titration. Introduced: 2020–12–01. Moscow : Standartinform, 2020. EM