*Environmental Engineering and Management Journal* April 2019, Vol. 18, No. 4, 929-933
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

*"Gheorghe Asachi" Technical University of Iasi, Romania*

# DETERMINATION OF COAL MICROELEMENTS BY INSTRUMENTAL ANALYSIS

**Cristian Tomescu***, **Cornel Boantă, Nicolae Ianc, Adrian Matei, Razvan Dragoescu**

*National Institute for Research and Development in Mine Safety and Protection to Explosion – INSEMEX Petroşani, 32-34 G-ral Vasile Milea Street, 332047 Petroşani, Romania*

## Abstract

In the mineral matter of coal there are microelements chemically bounded to organic matter or mineral impurities in various combinations that catalyzes the evolution / involution of a spontaneous combustion phenomenon as an accelerator in the oxidation reaction or which slows down these processes.

Specialised literature analyzes the phenomenon of coal self-heating based on several theories of which we exemplify the theory of coal oxidation, the theory of pyrite and the theory of the microelements role in the process of coal oxidation.

For the determination of these microelements in coal, the inductively coupled plasma atomic emission spectrometry method by means of which the mineral concentrations of hard coal and lignite samples were determined.

The present paper proposes to perform a comparative analysis of the results obtained by laboratory determinations on samples taken from various coal basins (Valea Jiului, Motru, Jilt, Rovinari, Berbesti).

*Key words:* coal, instrumentation, microelements, oxidation, tests

*Received: September, 2018; Revised final: January, 2019; Accepted: April, 2019; Published in final edited form: April, 2019*

## 1. Introduction

Spontaneous combustion remains the major risk factor for coal exploitation depending of the extraction method applied. The development (evolution) or the involution of spontaneous combustion depends on the intervention method in exploiting process, on the technical and organizational measures provided in the working monograph (Matei et al., 2003; Tomescu et al., 2017).

The cause of the occurrence of the phenomenon, treated by the theory of microelements from coal and their role in the oxidation process, assumes the knowledge of the concentrations of the transitional paragenetic metals existing in its structure. International engineering practices use various technologies for chemical analysis and detection of microelements from coal, such as: Inductively coupled plasma atomic emission spectroscopy (ICP-AES), Laser Induced Breakdown Spectroscopy (LIBS) or X-ray photoelectron spectroscopy (Karayigit et al., 2000; Noel et al., 2007; Song et al., 2008). The paper follows the laboratory determinations by instrumental analysis of coal metals, on samples of coal, taken from 6 mining units in the Jiu Valley (Lonea, Livezeni, Vulcan, Paroseni, Lupeni and Uricani), as well as on samples of lignite from 6 productive capacities in the Jilţ, Motru and Berbeşti basins (mining quarries, Rovinari, Jilţ, Tismana, North Pesteana, Motru-Lupoaia and Berbeşti). The technical-material basis of National Institute for Research and Development in Mine Safety and Protection to explosion-INSEMEX Petroşani and the infrastructure of the Physico-Chemical Analysis Laboratory was the logistic support of the research activity within the work for this paper.

* Author to whom all correspondence should be addressed: e-mail: cristian.tomescu@insemex.ro; Phone/ Fax: +40 254546277

## 2. Material and methods

### *2.1. Experimental part*

From operational mining units 33 coal samples were sampled and processed for testing, 14 of which are hard coal and 19 are lignite, sampled from 33 coal beds. The selection of the samples was carried out by successive reduction to one quarter of the sampled quantity. Samples were subjected to grinding and sieving to a certain granulation, drying, weighing and dissolution.

Tests comprised two experimental stages on the coal self-ignition risk and determinations of micro-elements from the structure of analysed coal.

### *2.2. Risk of self-ignition of hard coal and lignite*

Self-ignition of coal represents a particular risk in mining industry and appealing to this notion used in the management of health and safety at work, the risk of self-ignition of the mineral substances, is classifying (Table 1) the carbonaceous substance in relation to the method of determining the laboratory, which corresponds to a function of classification (Tomescu, 2015):

- method of determining the risk of self-ignition in gaseous oxygen environment with classification function: the temperature gradient ΔT/20′;
- method of determining the risk of self-ignition in a liquid medium (perhydrol) function classification: the reaction rate $v_r$ ($^0$C / min) (Matei et al., 2004).

### *2.3. Instrument and method for laboratory analysis*

Carbon microelements are identified by the inductively coupled plasma atomic emission spectrometry method, an analytical procedure using Optima 2100 DV, Perkin Elmer Spectrometer. The principle of the method is the measurement of atomic emission by optical spectrometry. The substance of interest in the liquid state is nebulized and the resulting aerosol is carried by a gas stream (Argon) to the plasma torch. The characteristic atomic emission spectral line is produced by inductively coupled plasma (ICP). The radiation intensity that is proportional to the concentration of the element in the sample is recalculated internally from a set of calibration curves stored in the memory and is presented directly in the form of percent concentration.

## 3. Results and discussion

### *3.1. Tests on self-ignition risk*

The hard coal and lignite samples taken from the underground and quarrying facilities were first processed for tests of self-ignition risk testing by the two mentioned methods, with an ultra-thermostat, modernized with a temperature controller and pump recirculation of heating fluid, Dewar vessel with magnetic stirrer, high precision electronic thermometers. By interpreting temperature-time diagrams, obtained, temperature gradient and reaction velocity, the hard coal is classified as low, medium and high-risk self-flammable coal, and lignite is classified as medium-risk self - flammable coal and self-ignition. Examples of diagrams of temperature variation curves are given in Fig. 1 (hard coal) and Fig. 2 (lignite).

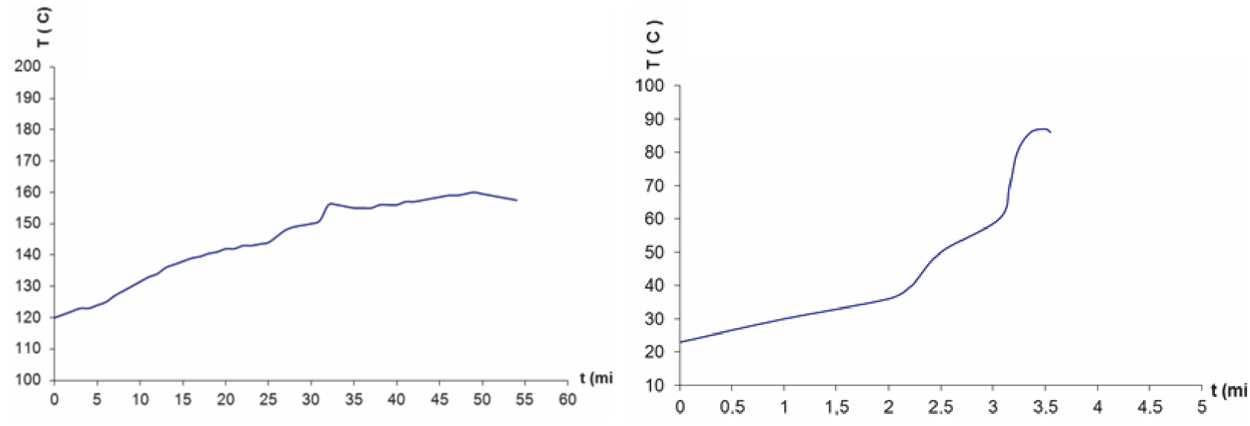
### *3.2. Tests on hard coal samples*

From the underground productive capacities, 14 samples of coal from exploitable layers 3 and 13 from 6 mining operations were collected and processed. In the first stage, the risk of self-ignition and classification from this point of view was determined. The determinations were performed according to the Physicochemical Analysis Laboratory test procedures ("Metal Determination" and "Digestion (Extraction) of Solids").

By means of spectrometric instrumental analysis, 10 microelements were identified in the mineral substrate (coal): As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Zn. The results obtained with the mean values of the element content are depicted in decreasing order of the concentration values in Tables 2, 3 and expressed in [mg/kg] or [g/t].

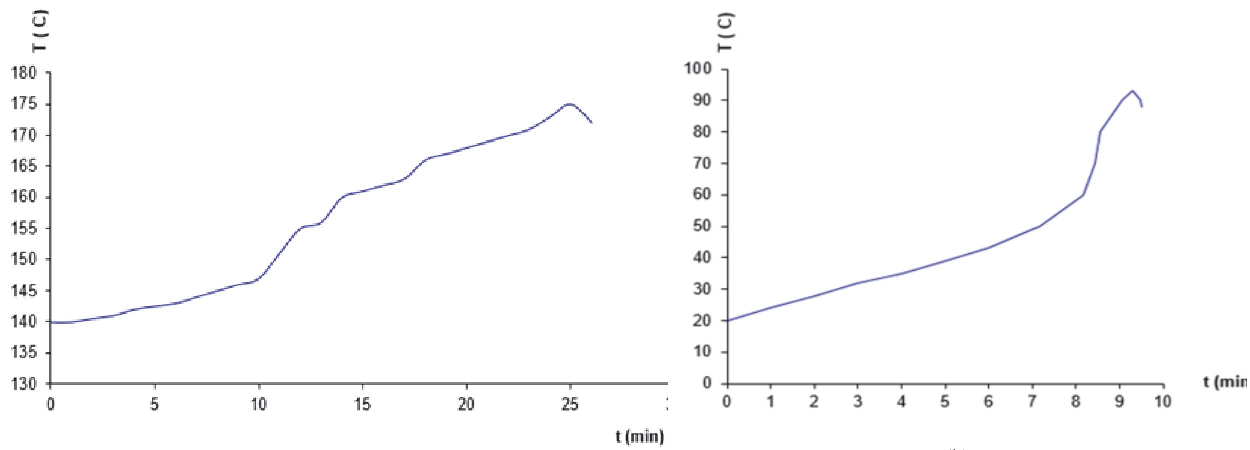
**Table 1.** Classification of coal at the risk of self-ignition (Tomescu et al., 2016)

| ***Group classification*** | ***The behaviour of coal*** | |
|---|---|---|
| | In gaseous oxygen environment / the temperature gradient ΔT/20′ | In a liquid medium (perhydrol) / the reaction rate $v_r$ ($^0$C / min) |
| **Group I** | Coal without risk of self-ignition, ΔT/20′ < 5°C/20′ | Coal without risk of self-ignition, $v_r$ < 3°C/min |
| **Group II** | Coal with low risk of self-ignition, 5°C/20′ ≤ ΔT/20′ ≤ 20°C/20′ | Coal with risk of self-ignition, 3°C/min ≤ $v_r$ ≤ 10°C/min |
| **Group III** | Coal with medium risk of self-ignition, 20°C/20′ ≤ ΔT/20′ ≤ 35°C/20′ | Coal with pronounced risk of self-ignition, $v_r$ >10$^0$C / min |
| **Group IV** | Coal with high risk of self-ignition, 35°C/20′ ≤ ΔT/20′ ≤ 50°C/20′ | - |
| **Group V** | Coal with pronounced risk of self-ignition, ΔT/20′ > 50°C/20′ | - |




(a) (b)

**Fig. 1.** Diagram of temperature variation curves for hard coal:
a) the curve of oxidation of coal with oxygen in the gaseous environment for slaughter undermined front bench no. 23/3 / II, subfield III, Lonea Mining; b) the curve of temperature at oxidation of coal with oxygen in the liquid environment for slaughter undermined front bench no. 23/3 / II, subfield III, Lonea Mining




(a) (b)

**Fig. 2.** Diagram of temperature variation curves for lignite: (a) the curve of oxidation of coal in gaseous environment for Jilt Mining quarrier; (b) the curve of oxidation of coal in liquid environment for Jilt Mining quarrier

### *3.3. Testing of lignite samples*

Following the same steps as for the determination of the microelements in the hard coal, the tests on 19 lignite samples taken from the exploitable layers 1-14 from the 6 quarries identified 10 microelements.

**Table 2.** Microelements in the hard coal

| ***No.*** | ***The element*** | ***Content elements in the hard coal [mg/kg] or [g/t]*** | | |
|---|---|---|---|---|
| | | $c^*_m$ | $C^*_M$ | $C^*_{med}$ |
| 1. | Iron | 4048 | 25120 | 11775 |
| 2. | Titanium | 119.7 | 540.4 | 321.66 |
| 3. | Nickel | 33.3 | 304.5 | 84.24 |
| 4. | Copper | 28.83 | 100.6 | 52.83 |
| 5. | Chromium | 19.30 | 75.10 | 45.22 |
| 6. | Zinc | 23.87 | 65.17 | 39.70 |
| 7. | Manganese | 5.903 | 96.79 | 33.45 |
| 8. | Arsenic | 3.641 | 125.6 | 32.63 |
| 9. | Lead | 5.66 | 42.47 | 20.28 |
| 10. | Cobalt | 2.78 | 54.93 | 16.72 |

*Note:* $c^*_m$, $C^*_M$, $C^*_{med}$ *= minimum, maximum and average content elements*

The same test procedure as in the case of hard coal samples was followed. As in the case of hard coal, the average values of the element content are shown in descending order of the concentration values in the Table 2, and lignite in the Table 3.

**Table 3.** Microelements in the lignite

| ***No.*** | ***The element*** | ***Content elements in the lignite [mg/kg] or [g/t]*** | | |
|---|---|---|---|---|
| | | $c^*_m$ | $C^*_M$ | $C^*_{med}$ |
| 1. | Iron | 4117 | 20680 | 9146.74 |
| 2. | Titanium | 50.66 | 683.5 | 227.6 |
| 3. | Manganese | 44.05 | 110.05 | 98.88 |
| 4. | Cooper | 14.71 | 71.82 | 32.31 |
| 5. | Zinc | 9.12 | 69.35 | 26.03 |
| 6. | Chromium | 4.57 | 48.11 | 45.22 |
| 7. | Arsenic | 0.24 | 73.26 | 18.84 |
| 8. | Nickel | 5.57 | 29.55 | 15.25 |
| 9. | Lead | 0.42 | 19.09 | 4.96 |
| 10. | Cobalt | 0.36 | 10.5 | 2.19 |

*Note:* $c^*_m$, $C^*_M$, $C^*_{med}$ *= minimum, maximum and average content elements*

The results of measurements of the microelement content in successive determinations have a deviation of ± 5 %. By accessing on-line specialized literature for comparing the test results with the ones obtained by international researchers were identified hard-coal and brown coal analysis works on 300 samples from EU countries (Stepien et al., 2008).

### *3.4. Comparative analysis*

It was found that predominantly in the coal is iron, followed by titanium, manganese, copper, zinc, chromium, arsenic, nickel, lead and cobalt, determined in the tests for hard coal. With small differences in the content of metals in which the largest share is iron, for the lignite tests the scale resembles that of the hard coal, the first and last two positions being occupied by the same elements.

By resorting to coal petrography, these microelements in the form of the ions are found in the most reactive component of the coal-humid, which is chemically formed of humic acid and humic substance, which has strong absorption and ion exchange properties, and possibly concentrating on the ions of the ions and forming complex combinations in the oxidation mechanism (Panaitescu, 1991).

However, it should be kept in mind that the microelements are not uniformly dispersed in the coal bed, an argument being that in the tests one of the elements, such as chromium, was undetectable, leading to the finding that the physicochemical mechanisms oxidation that occurs in the development of spontaneous combustion, the complex oxygen transport combinations are influenced differently by the reaction with molecular oxygen in the air (Tomescu, 2017).

## 4. Conclusions

INCD-INSEMEX Petroșani research infrastructure is accredited and equipped with logistics for determining microelements from coal, using Inductive Coupled Plasma spectrometry, technology aligned with international engineering practices. Industrial and applicative research from the current article focused on the determination of these elements in coal, starting from the fact that their presence in micro quantities is a factor favouring the mechanism of spontaneous combustion.

The analysed coal, hard-coal and lignite from mineral deposits from coalfields using different exploitation technologies (underground and quarry) are predisposed to the risk of self-ignition. The paper does not address the phenomenon itself, but is considered as a support of the need of research on microelement determinations.

By laboratory instrumental analysis and the inductively coupled plasma atomic emission spectrometric method, the tests on coal and lignite samples taken from underground mining productive capacities and surface area resulted in the determination of elements found in micro amounts in the coal bed.

The 10 microelements determined in coal and lignite are: As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Zn, whose ions form complex combinations in the coal structure. On an ordered scale of 1 to 10, based on the average content, the predominant element in the coal bed is iron, both for coal and lignite. The results of the determinations are comparable to the results obtained by researchers from EU specialized institutes.

The results of the research led to the widening of the range of methods for preventing / combating the occurrence of spontaneous combustion phenomena and the self-induction of coal deposits of the power stations. The use of existing and improved laboratory methods and methodologies and increased expertise in the domain.

Knowing and understanding the kinetics of coal-carbon oxidation reactions and physicochemical factors which contribute to the development of a spontaneous combustion phenomenon offer the possibility of identifying solutions for preventing and combating this phenomenon and increase the security of the mineral resources and implicitly the health and safety of workers of the mining industry.

**Acknowledgement**
This paper was developed within the Nucleu-Programme, carried out with the support of the Ministry of Research and Innovation - MCI, project no. PN-16-43-02-02.

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