

## Pyrohydrolytic determination of fluorine in coal: A chemometric approach

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### ABSTRACT

Corrosion effects in thermal power plants and environmental impact cause an increase in demand for fluorine analysis in coal. Solid sample decomposition, organic and inorganic fluorine compounds, volatility of fluorine species are problems which deserve a special attention. The aim of this work was to optimize the pyrohydrolytic (Phy) determination of fluorine content in the lignite coal. The parameters of pyrohydrolysis were evaluated and optimized by two statistical methods: Plackett–Burman (PB) design and response surface methodology (RSM). The content of fluorine in the absorption solution was measured by fluoride ion-selective electrode. The limit of detection of the proposed method was  $20 \mu\text{g g}^{-1}$ , with good recovery (95%) and relative standard deviation less than 5%. With such benefits as simplicity, precision, accuracy and economy, this method is highly suitable for routine analysis of coal.

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### 1. Introduction

Coal is one of the most important sources of energy and its worldwide use will continue to expand during the next several decades. However, the combustion process produces a huge amount of gas and solid waste products which cause environmental problems [1–3]. In recent years, many toxic trace elements including fluorine in coal attracted much attention [4–6]. In this paper, composite coal samples from Kolubara basin, Serbia, were used and investigated for fluorine content.

Fluorine is one of the most abundant trace elements in coal, with the concentration range for most coals from  $20\text{--}500 \mu\text{g g}^{-1}$ , with a mean value of  $150 \mu\text{g g}^{-1}$  [7]. During coal utilization a large amount of toxic compounds of fluorine such as HF, SiF<sub>4</sub> and CF<sub>4</sub> [8], are released into atmosphere, leading to harmful effects on environment and human health. From this point of view, it is important to establish accurate, precise and reliable method for determination of this element.

Although there are a few instrumental methods [9,10], the quantitative determination of fluorine in coal has been usually carried out after dissolution or combustion of coal to make fluorine solution. For this purpose, methods such as distillation, alkali-fusion, bomb combustion and pyrohydrolysis have been used [11–17]. Some of these methods are complex and time consuming, may give incomplete breakdown of the fluorine-containing components, or

lead to loss of the element by volatilization if the fusion temperature is not carefully and accurately controlled [18].

Procedure using bomb combustion of the coal is standard method for the determination of fluorine in coal [19]. However, pyrohydrolysis is acknowledged as the most common standard method for the determination of fluorine in coal (ISO 11724:2004, ASTM D5987-96, GB/T 4633-1997). Pyrohydrolytic method provides accurate results for fluorine in coal, but requires considerable skills in its application and complex apparatus [15]. Pyrohydrolysis and bomb combustion are usually followed by fluoride ion-selective (F-ISE) method or ion chromatography (IC). Proton-induced gamma-ray emission (PIGE) is non-destructive technique with lowest detection limit [10]. The main disadvantage of this method is limited access to the instrumentation. In this work fluoride concentration in absorption solution was measured with fluoride ion-selective electrode (F-ISE).

The pyrohydrolysis procedure for fluorine determination was first proposed by Warf et al. [11]. In this procedure, steam was passed over a heated sample in a platinum apparatus and the volatile products of the pyrohydrolysis were condensed and titrated. Several authors have reported on the use of pyrohydrolysis to determine the fluorine content of various inorganic materials, but only the reaction conditions seem to differ to a large extent [12–15]. The platinum reactor tube in Warf's apparatus has been replaced by nickel, quartz and ceramic. Samples were heated in tube [12,13] or induction furnaces [14], or by burners [15]. In general, pyrohydrolysis has been carried out in the presence of a catalyst [12–14]. An oxidant carrier gas [14], saturated with water vapor, or mixture of air and water vapor [15], is passed over a heated

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**Table 1**  
Proximate and ultimate analysis of composite coal samples.

Samples	Proximate analysis (wt%, dry basis)				Ultimate analysis (wt%, dry basis)				
	Moisture	Ash	VM	FC	C	H	N + O*	S	Calorific value (kJ kg <sup>-1</sup> )
EPS1	20.7	28.4	41.6	30.0	46.6	4.07	20.7	0.72	18 807
EPS2	24.6	25.0	44.2	30.8	48.9	4.27	21.7	0.82	19 420

\* The content of N and O is given as a sum (according to programme of CHNS Analyser, Perkin Elmer 2400).

sample and the hydrogen fluoride evolved is collected in diluted alkali or simply condensed.

The aim of this paper was to examine the influence of large number of parameters on fluorine release from coal during pyrohydrolytic decomposition. Using design of experiment (DOE) approach, the resulting data can identify the most influential factors, the synergism between factors and optimal conditions [20–24]. Multifactorial experiments, in general, are performed for diverse applications when checking significant influences before optimization procedures is priority. The choice of experimental design (full factorial, fractional factorial, response surface, etc.) depends on the number of parameters (variables). The parameters of pyrohydrolysis in this work were evaluated and optimized by two statistical methods: Plackett–Burman (PB) design and response surface methodology (RSM). PB design has been confined to main effects and it can be applied only in the cases when there is no interaction between parameters. The RSM as a statistical modeling technique was employed for multiple regression analysis using the data obtained from PB designed experiments. In this work the PB experimental design with seven variables (parameters), at two levels, in eight runs, was used to optimize the pyrohydrolytic determination of fluorine.

## 2. Experimental part

### 2.1. Chemicals and solutions

All solutions were prepared using distilled/deionized water (18 MΩ cm). All chemicals were of analytical grade quality.

#### 2.1.1. Vanadium pentoxide

Ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) from Merck was heated in platinum crucible between 500 and 550 °C until the product obtained (V<sub>2</sub>O<sub>5</sub>) became dark red (ca. 4 h) [25].

#### 2.1.2. Total ionic strength adjustment buffer (TISAB) solution

The 58 g of sodium chloride (Merck), 4 g of 1,2-diammine-cyclohexanetetraacetic acid (Merck) and 57 mL of acetic acid (Merck) were dissolved in 500 mL of water. After dissolution the pH was adjusted to 5.2–5.5 with 5 M sodium hydroxide (Merck) solution and the volume was adjusted to 1000 mL by addition of water.

#### 2.1.3. Standard fluoride solution for ISE measurement

2.210 g of sodium fluoride (Merck) dried for 2 h at 105 °C was dissolved in water and diluted to 1000 mL. The solution was stored in polyethylene bottle. Fluoride calibration solutions in range of 0.1–10 μg mL<sup>-1</sup> were prepared by serial dilutions of standard solution with water.

**Table 2**  
Macro and micro components analysis of composite coal samples.

Parameter	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	TiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
	(wt%, dry basis)									
EPS1	54.5	24.2	2.02	6.55	0.32	0.64	0.41	6.34	6.34	<0.01
EPS2	54.4	21.9	2.24	8.84	0.62	2.18	0.80	8.19	0.62	<0.01

### 2.2. Coal samples

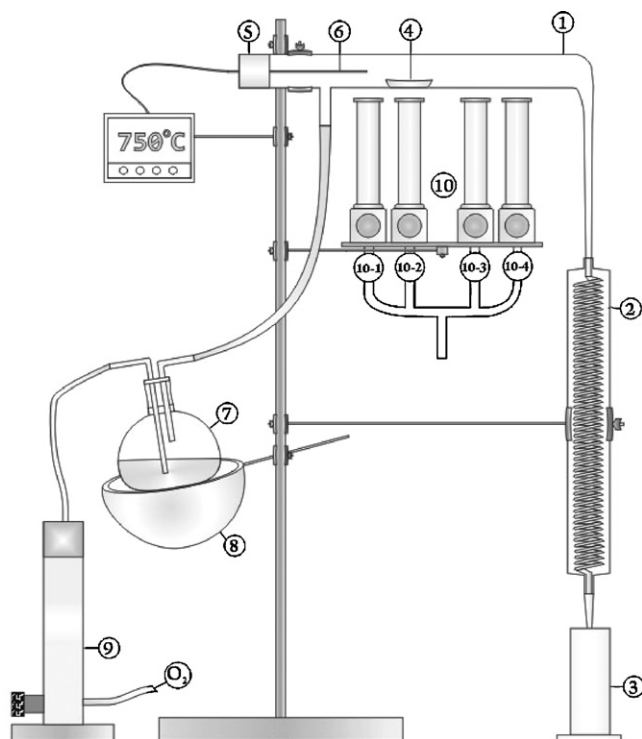
Twenty coal samples were collected from the Tamnava-West field, coal field Kolubara, Serbia. The Tamnava-West field, coal field is the part of Kolubara mining district and is located in the western part of the basin Kolubara. The Kolubara basin lies some 40 km south of Belgrade and is approximately 300 km<sup>2</sup> in extend. Coal exploitation in Tamnava-West field, coal field commenced 10 years ago. In this study all samples were collected from drilling hole, which depth was 60.2 m. The samples were grounded in a mill and finally in an agate mortar in order to obtain particle sizes ≤200 mesh.

The PB experiments were performed with in-house prepared composite samples of Kolubara's coal. The results of proximate and ultimate analysis obtained in inter-laboratory analysis are shown in Table 1. Table 2 presents the results of macro and micro component analysis. For the lignite coal of Kolubara basin is characteristic the presence of highly volatile matters, high moisture and low sulfur content, moderate ash yield and high calorific value. Fluorine content in composite coal samples was determined with standard method [26]. Fluorine content in composite sample denoted as EPS1 was 167 μg g<sup>-1</sup> and in composite sample denoted as EPS2 was 150 μg g<sup>-1</sup>. The proposed method was validated by the determination of fluorine concentration in certified reference materials BCR 460 (European Commission, Measurements and Testing Programme) and NIST 1632c (National Institute of Standards and Technology, USA) coal samples. Applicability of the method was tested by analyzing real coal samples from the Tamnava-West field, coal field.

### 2.3. Analytical procedure

#### 2.3.1. Pyrohydrolysis apparatus and procedure

The in-house made pyrohydrolysis apparatus is illustrated in Fig. 1. It consists basically of a steam generator unit, burners, a condenser, a collector for the fluoride distillate and pyrohydrolysis unit. The pyrohydrolysis unit consists of quartz (reaction) tube and quartz boat. The quartz tube is curved on one end and connected to the condenser through a silicone rubber stopper. Quartz boat with sample introduces the reaction tube on the other end. Once quartz boat is placed in quartz tube, inlet is closed with rubber stopper through which temperature sensor passed. The steam generator is round bottom flask with distilled water, which is immersed in heating mantle. The round bottom flask is adapted to a flow meter, which regulated gas flow. Gas (Ar or O<sub>2</sub>) passes through flow meter, mixed with water steam and reached the pyrohydrolysis unit. The inlet of gas/steam mixture is placed 3 cm from left side of pyrohydrolysis unit. The quartz tube is heated by four burners. The cold condensed solution contain-



**Fig. 1.** Apparatus for pyrohydrolysis of coal samples. Legend: (1) quartz tube ( $L=200$  mm, i.d. = 15 mm); (2) condenser; (3) polypropylene vial (50 mL); (4) quartz boat ( $L=17$  mm, width=9 mm, depth=6 mm); (5) rubber stopper; (s6) temperature sensor; (7) round bottom flask (250 mL); (8) heating mantle; (9) flow meter ( $50\text{--}500$  mL  $\text{min}^{-1}$ ); (10) (1–4), heaters.

ing the analyte is collected into a 50 mL graduated polypropylene vial.

Under quartz tube four heaters were placed on appropriate holder in order to steadily pyrohydrolyse the sample. The burner (10-1, see Fig. 1) was placed next to gas/steam inlet to prevent steam condensation and sample wetting. Second burner (10-2) was prime heater since quartz boat with sample was placed above it. The burners (10-3) and (10-4) ensured equal heating of quartz tube and burned organic vapor which intensively evolved at the beginning of pyrohydrolysis.

Pyrohydrolysis provides an elegant, simple procedure for the separation of fluorine from solid matrix. Several experimental parameters were found to be critical for success of used method [27]. In this paper the influence of various parameters to pyrohydrolysis as first step for fluorine determination in coal was investigated in details. The following parameters were tested: temperature, time, reaction atmosphere ( $\text{O}_2$  or Ar), gas flow, a catalyst, type of absorption solution and steam flow rate. The apparatus for pyrohydrolysis with all its parts is shown in Fig. 1. For detailed investigation two composite coal samples were used and they were labeled as EPS1 and EPS2. The coal sample EPS1 was composite coal sample from Kolubara basin, Serbia. The coal sample EPS2 was composite coal sample from Kostolac, Serbia. In some experiments to the composite coal samples catalyst was added, in that case the mass of catalyst was measured directly in quartz boat. The boat (4, see Fig. 1) containing the sample or catalyst/sample mixture was introduced into cold quartz tube (1, see Fig. 1). The boat was placed above the burner, 10-2, as shown in Fig. 1. Subsequently, the rubber stopper with temperature sensor was inserted into quartz tube. The polypropylene vial (3) with 15 mL of absorption solution was placed underneath the condenser. At this point water in round bottom flask boils (gently or intensively, depending of experimental conditions). Gas flow rate was set, allowing gas to mix with

steam, but not entering the quartz tube. Burners, (10-1, 10-3 and 10-4, see Fig. 1) were ignited at the same time and round bottom flask was closed, which allowed gas/steam mixture to enter the quartz tube. Moment when the burner, 10-2, was ignited is the starting time for pyrohydrolysis. Experimental conditions for each pyrohydrolysis reaction are given and discussed further in the text. At the end of decomposition of sample, quartz tube was washed with deionized water and collected in vial. Solution from vial was diluted to 100 mL and stored in polyethylene bottle. Fluorine concentration was measured potentiometrically with ISE. A blank for the composite sample consisted of either a boat containing catalyst or empty boat. A blank was run prior to the sample used for each pyrohydrolysis experiment.

After the sample pyrohydrolysis the quartz tube was washed with acetone, rinsed with water and dried. The quartz boat was soaked in 1 + 1 nitric acid/water solution for 10 min. Finally, it was rinsed with water and dried.

### 2.3.2. Fluoride determination

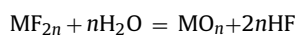
All potentiometric measurements were done on pH-ion meter C863 (Consort, Belgium) with a combination fluorine ISE electrode (ISE27B). Aliquot (25 mL) of pyrohydrolysed solution was diluted 1:1 with TISAB solution and the electrode potential ( $E_1$ ) was recorded. After recording the potential, solution was spiked with 1 mL of  $25 \mu\text{g mL}^{-1}$  standard fluoride solution and new electrode potential was recorded ( $E_2$ ). Calibration curve was prepared by measuring potential in standard fluoride solutions, which was diluted 1:1 with buffer solution. A graph of mV versus log concentration was prepared and electrode slope constant ( $S$ ) was calculated. Fluoride concentration in pyrohydrolysate was obtained from potential difference between spiked and unspiked solutions and slope constant as described [28], and concentration of fluorine in the coal samples was calculated. Standard addition method for fluoride ISE measurement was selected in order to insure fast and sensitive electrode response and to avoid the interferences of different type of matrix (differences between standard and pyrohydrolysate solutions).

### 2.4. Experimental design

As suggested in Section 2.3.1 the influence of seven parameters on pyrohydrolytic determination of fluorine in coal were investigated. Since many variables were involved, experimental design are powerful tools for the optimization of analytical procedures. Among the different groups of design, the PB factorial design allows the effects of a great number of variables to be known with relatively few experiments [29].

Two levels for each selected parameters are shown in Table 3. Usually, the minimum and the maximum possible level values are selected for screening experiments (denoted as  $-1$  and  $+1$ , in Table 3).

The general reaction of pyrohydrolysis can be expressed as:



**Table 3**  
Experimental factors and levels of factors.

No.	Variable	Level -1	Level +1
1	Temperature	900 °C	1100 °C
2	Time	5 min	15 min
3	Gas flow rate	50 mL $\text{min}^{-1}$	300 mL $\text{min}^{-1}$
4	Atmosphere	Ar	$\text{O}_2$
5	$m(\text{V}_2\text{O}_5)/m(\text{coal})$	0	4
6	Absorption solution	$\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$ , 20 mM
7	Steam flow rate	0.7 mL $\text{min}^{-1}$	2 mL $\text{min}^{-1}$

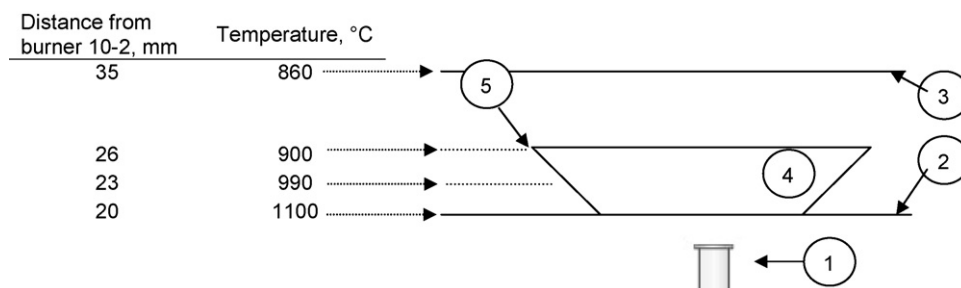


Fig. 2. Temperature gradient in quartz reaction tube. Legend: (1) heater 10-2; (2) lower quartz tube wall; (3) upper quartz tube wall; (4) quartz boat; (5) temperature control point.

Warf et al. [11] distinguished fluorides into two groups: a rapidly pyrohydrolyzable group and a slowly pyrohydrolyzable group. Many studies showed that the main chemical forms of fluorine in coal were of inorganic association [8,30,31], which belong to the latter group. Maximum pyrohydrolysis temperature was 1100 °C since this was maximum pyrohydrolytic temperature that could be achieved in apparatus shown in Fig. 1. In Fig. 2 the result of precise measurements of temperature gradient are presented. From Fig. 2 it is shown that the temperature in pyrohydrolytic unit depends on the position of temperature sensor and the position of burners. In all our experiments we had reached the temperature of 1100 °C which was appropriate [15] for total fluorine recovery.

Due to the complexity of coal composition and strong reaction capacity of fluorine, trace amounts of organic fluorine probably exist in coal, and the 900 °C was chosen as the minimum. The 1100 °C was achieved when quartz tube was placed at ca. 2 cm above the burner. On the other hand, 900 °C was achieved when quartz tube was placed ca. 4 cm above the burner. Since fluorine in coal existed mostly in inorganic compounds minimum pyrohydrolyse time was 5 min. Considering the constant sample mass (0.25 g) in all experiments maximum pyrohydrolysis time was reached after 15 min. Experiments were performed in inert and oxidant atmosphere. Liu et al. [32] showed that as oxygen concentration increases, the amount of fluorine emitted from coal increased. This was the reason why atmosphere flow rate was investigated between 50 and 300 mL min<sup>-1</sup>.

Regarding catalysts, vanadium pentoxide has been chosen as one of the most active within the process of decomposition of solid samples. Steam flow rate was investigated in gently (0.7 mL min<sup>-1</sup>) and intensively (2 mL min<sup>-1</sup>) water boiling conditions, since water vapor is one of the reactants in pyrohydrolysis equation. During the pyrohydrolysis, fluorine is volatilized as acid matter, HF, and after condensation it was absorbed in deionized water or sodium carbonate solution.

The amount of sample was 0.25 g. Sample was previously mixed with catalyst, when catalyst was used. The matrix of experiments obtained according to the PB design is shown in Table 4. The runs were performed in random order to assure that uncontrolled factors do not affect the results.

Table 4  
Plackett–Burman design, real values.

Exp.	Temperature (°C)	Time (min)	Gas flow rate (mL min <sup>-1</sup> )	Atmosphere	$m(V_2O_5)/m(\text{coal})$	Absorption solution	Steam flow rate (mL min <sup>-1</sup> )
P1	1100	5	50	Ar	0	Na <sub>2</sub> CO <sub>3</sub>	2
P2	1100	5	300	Ar	4	H <sub>2</sub> O	0.7
P3	900	15	50	Ar	4	H <sub>2</sub> O	2
P4	900	5	300	O <sub>2</sub>	0	H <sub>2</sub> O	2
P5	900	15	300	Ar	0	Na <sub>2</sub> CO <sub>3</sub>	0.7
P6	1100	15	50	O <sub>2</sub>	0	H <sub>2</sub> O	0.7
P7	1100	5	50	O <sub>2</sub>	4	Na <sub>2</sub> CO <sub>3</sub>	0.7
P8	900	15	300	O <sub>2</sub>	4	Na <sub>2</sub> CO <sub>3</sub>	2

### 3. Results and discussion

#### 3.1. Determination of fluorine in coal by Phy-ISE method

##### 3.1.1. Plackett–Burman (PB) design

The aim of experimental design was to identify the most influential factors on fluorine release from coal during pyrohydrolysis. According to data presented in Table 4 eight pyrohydrolytic experiments were performed and concentration of fluorine in absorption solution was measured using fluoride ISE. Subsequently, concentration of fluorine in coal was calculated and the results were analyzed using statistical software.

Two types of graphical display of data, Pareto charts and main effect plots were used to find a relationship between the input variables and the system responses. The change in response, produced by the change in the level of a variable, is the effect of that variable. The Pareto chart analyzes the magnitude and the importance of each variable effect. The length of bars in the chart is proportional to the standardized effect (estimated effect divided by its standard error). From this chart, absolute values of effects can be compared. The mean for a given level of variable is the average of all responses obtained for that level. So, the response means for each process variable level are plotted connecting the points for each process variable.

Fig. 3 shows a Pareto chart resulting from the statistical analysis of fluorine concentration in coal obtained by Phy-ISE method. Absolute values of gas flow, steam flow rate, catalyst and absorption solution effects indicated that these factors act in a negligible way on pyrohydrolytic decomposition of coal. During pyrohydrolytic decomposition of coal chemical bonds decompose and fluorine diffuse from matrix bulk forming hydrogen fluoride with steam. Those are the reasons why time has the greatest influence on pyrohydrolytic decomposition of coal. The influence of atmosphere on pyrohydrolytic release of fluorine from coal is somewhat greater than the influence of pyrohydrolysis temperature.

The main effect plot is useful to determine which process variables influence the response and also to compare the relative strengths of effects. The relative magnitudes of the process variable effects can be compared by comparing the slopes of the lines (the greater the degree of departure from horizontal, the stronger

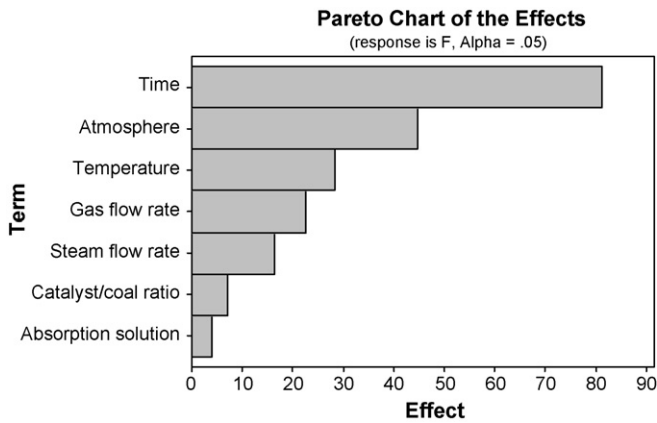


Fig. 3. Pareto chart for Phy-ISE combined method.

the effect). In contrast to the Pareto chart, which compares absolute values of effects, the main effect plot provides additional information on whether the change between two variable levels decreases or increases the response.

Main effect plots shown in Fig. 4 indicate that with increasing temperature and time of pyrohydrolysis, the amount of released fluorine from coal increase. Pyrohydrolytic decomposition of coal is followed with breaking of chemical bonds in fluorine organic and inorganic compounds. Since these processes are energy required it is clear why the fluorine releasing increases when temperature increases. PB design revealed, which is confirmed by Pareto chart that beside time, type of atmosphere had the biggest influence on fluorine emitting during pyrohydrolysis. It means that fluorine concentration in absorption solution increase in the presence of oxygen. Main effect plot (Fig. 4) showed that not only the feature of gas, but also the gas flow has positive influence on pyrohydrolytic fluorine release. These results are consequence of oxygen concentration, when it increases during coal combustion, the surface temperature of coal is higher than the average pyrohydrolytic temperature. This induces rapid decom-

Table 5  
Response surface design.

Exp.	Temperature (°C)	Time (min)	R (%)
1	950	14	58
2	800	2	48
3	800	14	71
4	950	2	44
5	800	26	72
6	950	14	60
7	1100	14	97
8	950	14	62
9	950	14	54
10	950	26	75
11	1100	26	98
12	950	14	64
13	1100	2	62

position of the inorganic substances, including fluorine in coal [30].

These screening experiments provided important information on pyrohydrolytic decomposition of coal, followed with fluoride ISE determination. Although all parameters were varied in a large scale, the type of absorption solution, utilization of vanadium pentoxide, as a catalyst, and velocity of steam generation had no significant influence on pyrohydrolytic determination of fluorine. The most important parameters on Phy-ISE determination of fluorine in coal were time, temperature and oxidation atmosphere.

### 3.1.2. Response surface methodology (RSM)

As an effective tool for the optimization of the fluorine decomposition process which is characterized by a combination of several independent variables, the Central Composite Design (CCD) as a part of RSM was applied. The RSM is a statistical modeling technique employed for multiple regression analysis using the data obtained from designed experiments. CCD is commonly applied as an economical way of obtaining the maximum amount of information with the fewest experiments [33,34]. A two factor CCD, with 5 center points, results in 13 runs is shown in Table 5. Factors and levels considered were: time (from 2 to 26 min) and temperature (from 800 to 1100 °C). The fluorine recovery (R, %) was calculated

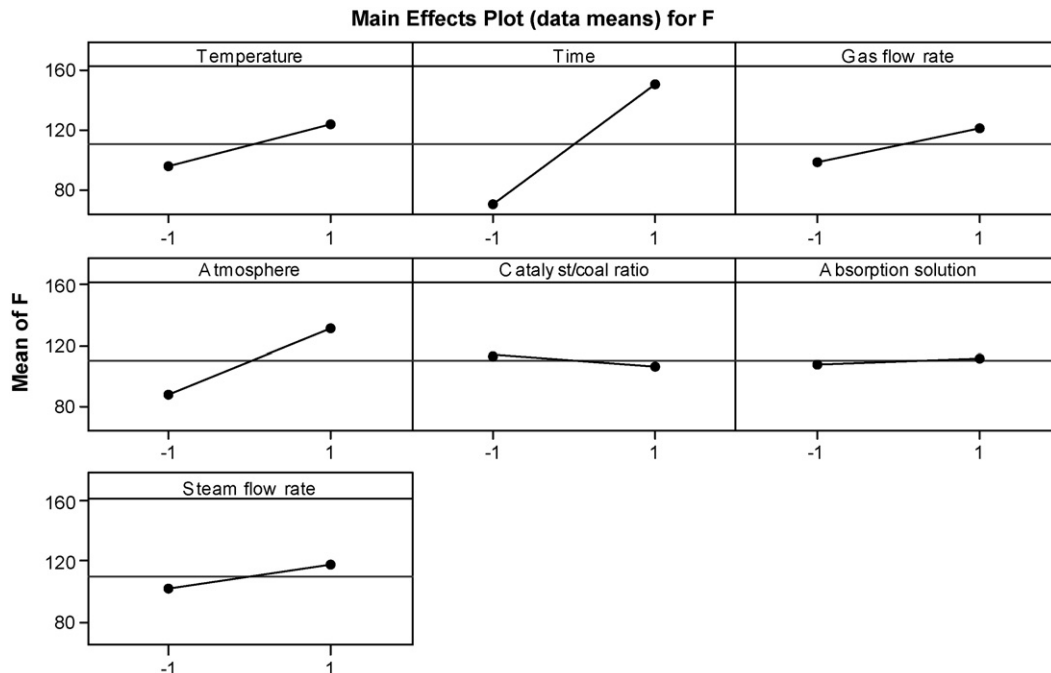
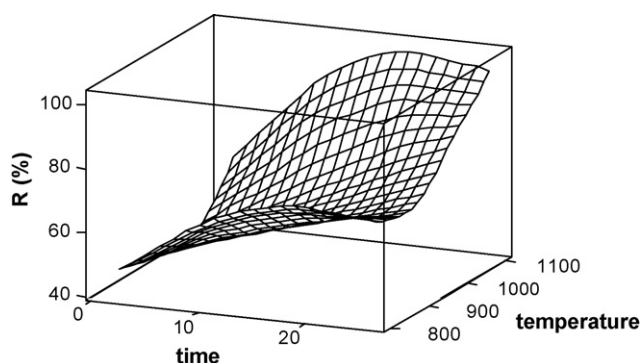


Fig. 4. Main effect plots.

**Table 6**  
Estimated regression coefficients for the response surface design.

Term	Coefficient	Standard error of the coefficient	p-value
Constant	61.448	2.171	0.000
Time (A)	15.500	2.135	0.000
Temperature (B)	11.333	2.135	0.001
A × A	-6.569	3.146	0.075
B × B	17.931	3.146	0.001
A × B	3.500	2.614	0.222

**Fig. 5.** Response surface for fluorine recovery as function of time (min) and pyrohydrolytic temperature (°C).

as a ratio [measured value]/[certified value]. The measured value was fluorine content for given experiment which is, also presented in Table 5.

The samples were pyrohydrolysed as described. It was observed that fluorine emission during pyrohydrolytic decomposition of coal is more efficient in oxygen atmosphere; therefore the oxygen was selected as constant for the further experiments. The oxygen flow rate was  $300 \text{ mL min}^{-1}$ , since the amount of fluorine released from coal increases with flow rate. As it is shown steam flow rate has no significant influence on pyrohydrolysis, but higher value of this parameter was selected ( $2 \text{ mL min}^{-1}$ ) in order to ensure the quantitative recovery of fluorine. Results presented in Fig. 4 revealed that the effect of vanadium pentoxide on fluorine decomposition is negligible and even slightly negative. Consequently, this parameter was selected to be avoided in further experiments. The volatile hydrogen fluoride acid, after condensation was absorbed in alkaline solution. In Table 6 are summarized the estimated regression coefficients from the linear, square and interactions model. ANOVA results are presented in Table 7 and the finale response surface is shown in Fig. 5.

The statistical models applied were suitable for predicting and optimizing of fluorine determination within the range of variables used. The obtained coefficient of variation was  $R^2 = 94.30\%$ , indicating high degree of correlation between the response and independent variables and high degree of fitting. The results shown in Tables 5–7 and in Fig. 5 confirmed that the fluorine concentration in absorption solution increases with temperature. Coal pyrohydrolysis on  $1100^\circ\text{C}$  provided fluorine release in short time period, and 100% fluorine recovery was achieved in 14 min. For pyrohydrolytic determination of fluorine in real coal samples maximum pyrohydrolytic time of 15 min was adopted.

**Table 7**  
Analysis of variance (ANOVA) for response surface model (coded units).

Source of variation	Degrees of freedom	Sequential sum of squares	Adjusted sum of square	Adjusted mean of square	F-value	p-value
Regression	5	3149.40	3149.40	629.88	23.04	0.000
Linear	2	2212.17	2212.12	1106.08	40.46	0.000
Square	2	888.23	888.23	444.12	16.25	0.002
Interaction	1	49.00	49.00	49.00	1.79	0.222
Residual error	7	191.37	191.37	27.34		
Lack-of-fit	3	132.17	132.17	44.06	2.98	0.160
Pure error	4	59.20	59.20	14.08		
Total	12	3340.77				

**Table 8**  
Parameters of the proposed method.

Parameters	Values
Temperature	$1100^\circ\text{C}$
Time	15 min
Gas flow rate	$300 \text{ mL min}^{-1}$
Atmosphere	$\text{O}_2$
$m(\text{V}_2\text{O}_5)/m(\text{coal})$	0
Absorption solution	$\text{Na}_2\text{CO}_3$ , 20m M
Steam flow rate	$2 \text{ mL min}^{-1}$

**Table 9**  
Determination of fluorine in composite coal sample and in certified samples ( $n = 5$ ; uncertainties are standard deviations).

Sample	Determined value ( $\mu\text{g g}^{-1}$ )	Certified value ( $\mu\text{g g}^{-1}$ )	RSD (%)
EPS1	$164 \pm 6$	167*	3.70
BCR 460	$210 \pm 10.7$	$225 \pm 6$	5.10
NIST 1632c	$75.70 \pm 3.5$	$72.7 \pm 6.8$	4.60

\* Determined with standard ASTM method [26].

**Table 10**  
Fluorine recovery in standard coal samples and coal samples spiked with standard fluorine solution.

Sample	Fluorine ( $\mu\text{g g}^{-1}$ )		Recovery (%)
	Expected value	Determined value	
S1	250	245	98
S2	334	325	97.30
BCR 460	225	210	93.30
NIST 1632c	72.7	75.7	104

drolisis on  $1100^\circ\text{C}$  provided fluorine release in short time period, and 100% fluorine recovery was achieved in 14 min. For pyrohydrolytic determination of fluorine in real coal samples maximum pyrohydrolytic time of 15 min was adopted.

### 3.2. Validation and application of Phy-ISE method

The analytical parameters of the whole method are shown in Table 8. The accuracy of this method was evaluated by determining fluorine in in-house prepared composite coal sample from Tamnava-West field (EPS1), and in referent coal samples with certified fluorine content (BCR 460, NIST 1632c). Table 9 summarises the analytical results for this three coal samples. The relative standard deviation (RSD) of five repeated analyses ranged from 3.70% to 5.10%, indicating that the precision was satisfactory.

Fluorine recovery was investigated in spiked composite coal sample. Fluorine concentration in samples was increased by adding the standard fluorine solutions. The fluorine content in one case was increased for 50% (S1), and in the other for 100% (S2). Samples were pyrohydrolysed in three repeated analyses and fluorine content in spiked coal was calculated. The results of the analysis are shown in Table 10, where it can be observed that good recovery was achieved.

The proposed pyrohydrolytic procedure followed with ISE determination of fluorine was applied for determination of fluorine content in real coal samples. Twenty coal samples collected from Tamnava-West field, coal field were analyzed. Fluorine concentration ranged from 20 to 505  $\mu\text{g g}^{-1}$ . Higher fluorine concentration in some real coal samples can be attributed to the sample characteristic which has higher ash content. According to Finkelman [35], the fluorine is preferentially bonded to the inorganic compounds of the mineral coal. The obtained results were in good agreement with this observation. With increased ash content in analyzed samples, the fluorine content in coal increased.

#### 4. Conclusion

The pyrohydrolysis apparatus was constructed, and the procedure was designed to make coal combust and hydrolyse steadily and completely. The pyrohydrolysis parameters were optimized by two statistical methods: Plackett–Burman (PB) design and response surface methodology (RSM). It was concluded that optimal parameters for determination of fluorine in coal were: 0.25 g of coal sample, 0.30 mL  $\text{min}^{-1}$  of oxygen flux, a temperature of 1100 °C, 15 min of pyrohydrolysis and  $\text{Na}_2\text{CO}_3$  (2 mmol  $\text{L}^{-1}$ ) as adsorption solution. The limit of detection was 20  $\mu\text{g g}^{-1}$ .

ISE determination of fluorine is convenient with relative standard deviation less than 5% and recovery more than 95%. This method, which combines pyrohydrolysis and ISE make possible the determination of the content of fluorine in coal samples from 20 to 500  $\mu\text{g g}^{-1}$ .

Phy-ISE method was confirmed to be accurate and precise. The method can be widely used for routine determination of fluorine in coal, because no expensive instruments are required and the cost of analysis is low.

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