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The Application of Statistical Methods in the Construction of a Model for Identifying the Combustion of Waste in Heating Boilers Based on the Elemental Composition of Ashes

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Abstract: Emission of air pollutants constitutes one of the major hazards to human health and life. Particulate matter and harmful gases emitted by residential heating, especially, occupy a significant position among the sources of air pollution. This paper presents the research results concerning the composition of ashes obtained from the combustion of fuel samples composed of wood pellets, eco-pea coal, and coal pellets (trade name—VARMO) with various admixtures of waste materials. The study stand was equipped with a boiler having a nominal power of 18 kW. Several of the most characteristic chemical elements identified in the ash were used as the basis to classify the combustion of waste. A model based on a statistical method was designed. Within the framework of the research, a statistical multivariate technique, discriminant analysis, was applied. The statistical model was constructed for two groups of ash samples and 19 chemical elements indicating their contamination. The high prediction power of the model and the validation (fitting was 90.00% and 85.19%, respectively) confirmed the possibility of the practical application of this proprietary method. It permitted identification of the markers (chemical elements) in the ash. It confirms that the fuel is combusted with the admixture of waste materials in a given boiler. Based on the analyses performed, it was found that from among the 19 elements, five, namely K, Ti, Zn, Ca, and Rb, were selected as the markers because they are characterised by the highest discrimination ability. In addition, they are the best indicators of the contamination level of the ash samples that were examined.

Keywords: waste combustion; mathematical model; air pollution; ashes; co-combustion

Citation: Widera, K.; Grabowski, J.; Smoliński, A. The Application of Statistical Methods in the Construction of a Model for Identifying the Combustion of Waste in Heating Boilers Based on the Elemental Composition of Ashes. *Sustainability* **2022**, *14*, 11178. https://doi.org/10.3390/su141811178

Academic Editors: Ming Zhang, Yan Song and Hailin Mu

Received: 11 August 2022
Accepted: 5 September 2022
Published: 7 September 2022

1. Introduction

Limiting air pollution has become a key issue to be addressed concerning the quality of life of global populations [1,2]. Air pollution constitutes a problem that results from numerous indicators (i.e., urban development, industrialisation, road traffic, and inappropriate waste management) [3]. Additionally, apart from environmental damage, air pollution also exerts a significant negative impact on the economies, including adverse health effects [4–6]. The Upper Silesia Coal Basin (Poland) is characterised by the worst air quality; ten of the fifty European cities with the highest levels of air pollution are located in this region [7]. The main cause of poor air quality in the Upper Silesia Coal Basin is low emission originating from individual residential heating (domestic and communal emission), accounting for over 50% of particulate matter (PM_{10}) and about 90% of benzo(a)pyrene (BaP) emissions to the air [8]. The industrial and linear emissions of air pollutants have a significantly lesser impact. According to the Report of the European Environment Agency, it is estimated that about 45,000 deaths annually are caused by poor air quality [9].

By the same token, in the European Union, air pollution is considered to be the greatest hazard to the health of the EU residents. Approximately 400,000 people die every year due to the excessive levels of air pollution; the factor responsible for such a state of affairs is the exposure to exceeded admissible limits of $PM_{2.5}$, nitrogen dioxide, or ozone [10–12]. The populations of urban areas are especially exposed to the hazards connected with air pollution [10,13].

The East Asia Greenpeace Report also emphasises the importance of the global problem of air pollution [14,15]. According to the report, air pollution is conducive to the premature death of 3.2 mln to 6.2 mln people worldwide. The vast majority of the premature deaths, estimated at 2.3–3.7 million cases annually, are attributed to the exposure to $PM_{2.5}$. Ozone constitutes another air pollutant contributing to the premature deaths, accounting for 0.6–1.4 million cases. The third most significant contributor is nitrogen dioxide; exceeding its permissible concentrations in air is the cause of 0.3 to 1.1 mln deaths per year [15].

The emission of PM_{10} and hazard gases generated by boiler plants and household furnaces constitutes a significant source of air pollution in Central and Eastern Europe [16–18]. Frequently, fuels such as coal, wood, or biomass are combusted ineffectively, which means that the increased fuel consumption is incommensurate with the energy outcome, while the combustion processes are incomplete and fragmentary, thus creating an increase in the pollutants present in the exhaust gases. Inexpensive fuels of low heating parameters, e.g., floto-concentrates, coal slurries, or nonwoody types of biomass, are used, often with the admixture of different kinds of waste [19–24].

This is not only a problem in Poland; illegal incineration of waste in household heating furnaces is estimated at the level of 2–10% [25]. The major types of waste added to the fuel are wood residues, furniture, plastic materials, textiles, and tires. A similar situation takes place in Romania; research on air pollution in this country indicated that the combustion of waste results in an excessive emission of PM_{10} and polycyclic aromatic hydrocarbons (PAHs) to the atmosphere [26]. The fact that the price of basic fuels has recently been increasing worldwide allows for the assumption that the share of waste combusted in domestic furnaces may increase.

Eliminating the combustion of waste in household furnaces necessitates the design of rapid, efficient, and cost-effective detection methods to assess such practices. An analysis of the chemical composition of the exhaust gases seems to be the best analytical tool to identify the combustion or co-combustion of waste in individual heating appliances; based on characteristic markers, it is possible to detect the presence of prohibited materials added to the fuel [27–29]. Unfortunately, because it is necessary to sample the exhaust gases directly from chimney flues, the method cannot be applied in the case of combusting waste in domestic furnaces, particularly for consolidated chimney flue installations through which exhaust gases generated by various users are released.

The analysis of ashes appears to a promising alternative method to confirm the practice of combusting or co-combusting waste in individual household heating appliances. This method constitutes the best available tool to identify the above practices, and, more importantly, it is technically feasible [30]. Muzyka et al. [30] presented the analysis of the parameters of furnace waste combined with numerical classification methods. The classification analysis consists in examining the chemical composition of nine basic oxides, moisture, ash content, and ignition loss. The analysis comprises a set of logical rules and allows for classification of the examined sample to one of the three following classes:

- Class I: only pure fuel is combusted (the combustion of waste in the individual furnace is excluded);
- Class II: the combustion of waste in the individual furnace has not been identified;
- Class III: waste has been combusted in the individual furnace.

Grabowski et al. [27] applied for the first time statistical methods for the purpose of identifying fuels which were used in domestic heating, especially the ones with an admixture of waste. The application of hierarchical clustering analysis (HCA) [31–35] to interpret data concerning the chemical composition of ashes produced in the combustion of fuels and fuels blends with waste, organised in matrices, enabled identification of the similarities among the respective samples in parameter space together with the similarities among the measured parameters (content of the chemical elements in the ash) in the space of the samples [27].

This research constitutes an attempt to apply statistical methods to design a model that facilitates the classification of furnace combustion waste based on the presence of several of the most characteristic chemical elements identified in the post-combustion ash in individual furnaces. The objective of the research effort is to identify certain markers (chemical elements) that enable determining if the fuel used was burned with added waste in a given boiler. The markers (the elements) are selected by means of statistical methods from among the nineteen elements present in combustion waste.

2. Materials and Methods

The experiments on the co-combustion of fuel samples with various admixtures of waste materials were performed using a research stand including a boiler with a nominal power of 18 kW, 1.7 m^2 heating area, and 85% efficiency. The boiler was equipped with a 0.16 m^3 capacity automated underfeeder, an air heater installation for heat collection, and a measurement and control apparatus. The maximum working pressure of the boiler was 0.1 MPa, while the minimum chimney draught requirement was 16 Pa. The measurement system comprised a combustion process temperature regulator and an Itron CF 55 thermal efficiency meter. In addition, the research stand featured a measurement apparatus for determining the pollutants, including a type-S Pitot tube with an automatic dust meter, Emiotest 2598 (New York, NY, USA); DX-4000 Gasmet and Horiba PG350E (Vantaa, Finland) exhaust gas analysers (O_2, SO_2, NO, NO_2, CO, CO_2, H_2O); an LZO Signal 2000 analyser (Oldenburg, Germany), and a velocity aspirator with internal filtration. Figure 1 presents the schematic diagram of the research installation.

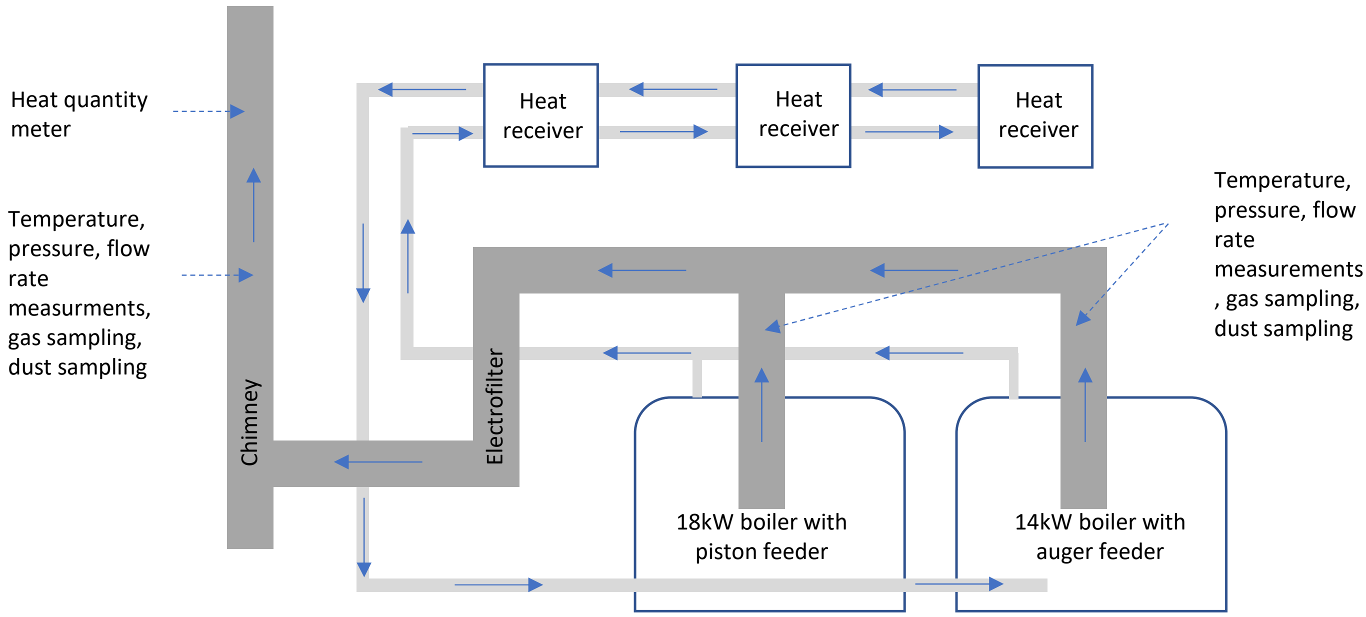

Figure 1. Schematic diagram of the research stand for combusting samples of fuels with the admixture of waste.

For the purpose of the study, the selected basic fuels, i.e., deciduous tree wood pellets, eco-pea coal, and VARMO pellets, were mixed (10:90 and 50:50) with the following waste materials: rubber, waste paper, RDF, MDF, plastic waste, textile waste, diapers, and multi-material packaging. Relevant physicochemical parameters of the fuel and waste samples in analytical state were determined. The combustion tests were performed by an accredited laboratory in the Department of Environmental Monitoring at the Central Mining Institute, Katowice, Poland.

The analytical moisture and ash content were determined using the weight method (according to the Polish standard PN-EN 15414-3:2011 and procedure SC-1.PB.03, respectively); total sulphur, carbon, and hydrogen were determined using the method of high-temperature combustion with IG detection according to standards PN-EN 15408:2011, PN-EN 15407:2011, and PN-EN 15407:2011, respectively. The heat of combustion and the calorific value were determined by means of the calorimetric method according to the standard PN-EN 15400:2011. The results are presented in Table 1.

Table 1. Analytical characterisation of the fuel, i.e., deciduous tree wood pellets (DTW), eco-pea coal (C), and VARMO pellets (V), and waste, i.e., rubber (R), waste paper (WP), RDF, MDF, plastic materials (PM), textiles (T), diapers (D), and multimaterial packaging (MMP).

Parameter	Unit	DTW	C	V	R	WP	RDF	MDF	PM	T	D	MMP
Total moisture	%*w*/*w*	4.62	6.63	1.81	1.92	2.86	4.16	4.68	2.81	2.66	2.81	2.64
Ash	%*w*/*w*	0.64	3.69	6.81	4.17	23.92	12.36	0.92	14.15	3.36	17.19	8.79
Carbon, C	%*w*/*w*	50.94	73.19	78.50	87.09	48.39	41.94	49.01	58.42	51.67	56.38	47.80
Hydrogen, H	%*w*/*w*	6.36	4.65	4.68	5.36	6.69	5.51	6.36	8.11	6.04	8.39	6.99
Total sulphur, S	%*w*/*w*	<0.03	0.56	0.31	1.31	0.21	0.07	<0.03	0.14	0.16	<0.03	0.07
Heat of combustion	kJ/kq	18,800	28,390	30,860	37,310	20,210	15,320	18,350	24,850	18,230	25,390	20,350
Calorific value	kJ/kq	17,420	27,390	29,860	36,170	18,780	14,110	16,970	23,110	16,920	23,600	18,830

During the course of the combustion tests, ash samples were taken in order to determine the contents of the following oxides: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SO_3, TiO_2, and P_2O_5, together with the contents of chemical elements, including heavy metals: Cl, Mn, Cu, Zn, Rb, Sr, Zr, Ba, and Pb. The analyses were performed using a Rigaku ZSX PRIMUS II wavelength dispersive X-ray fluorescence spectrometer. Discriminant analysis was used to construct the statistical model for the analysis of the elemental content of the ashes. Discriminant analysis constitutes a multivariate statistical tool applied to determine the set of rules enabling allocation of multiattribute objects to subclasses with the smallest possible classification error [36,37].

Numerous applications of this multivariate analysis tool are described in chemometric papers [38–41] and in research studies exploring the biodiversity of edible plants [42]. The analysis is also applied to create the algorithms of pattern classification [43], or errors in industrial processes [44]. Tahmasebi et al. [45] used this technique for the alteration separation of copper deposits, whereas Jia et al. [46] applied the method to detect flavonoids on the basis of gold nanoparticles. While constructing the model for the identification of chemical elements, which play the role of discriminant variables for the examined samples, the following components of the discriminant analysis were applied: (a) the linear discriminant function and canonical functions [47,48], which facilitate classification of objects (ash samples) to one of two groups; (b) the coefficient of discrimination λ (Wilks' lambda), which is used to evaluate the discriminatory power of the examined variables (the chemical elements) [49,50]; and (c) the statistical tests to validate the model based on Fischer distribution and χ^2. In this research study, the adopted level of statistical significance $\alpha = 0.05$.

3. Results and Discussions

In the study, the composition of ash coming from the combustion of the basic fuels (deciduous tree wood pellets, eco-pea coal, and VARMO pellets) and the fuels blended with the waste was studied. The data were organised into a matrix **X** (57 $\times$ 19), where the rows correspond to the samples of fuels/waste (see Table 2), whereas the columns characterise the examined parameters (see Table 3). The sample list of the mixtures composed of the basic fuels and waste is presented in Table 2.

Table 2. List of the fuel mixtures.

Fuel Mixture Number	Fuel Mixture Composition
1	Pellets
2	Pellets—90%/MDF *—10%
3	Pellets—50%/MDF—50%
4	Pellets—90%/RDF **—10%
5	Pellets—50%/RDF—50%
6	Pellets—90%/Textiles—10%
7	Pellets—50%/Textiles—50%
8	Pellets—90%/Waste paper—10%
9	Pellets—50%/Waste paper—50%
10	Pellets—90%/Plastic materials—10%
11	Pellets—50%/Plastic materials—50%
12	Pellets—90%/Rubber—10%
13	Pellets—50%/Rubber—50%
14	Pellets—90%/Multimaterial packaging—10%
15	Pellets—50%/Multimaterial packaging—50%
16	Pellets—90%/Diapers—10%
17	Pellets—50%/Diapers—50%
18	Pellets—90%/Construction waste—10%
19	Pellets—50%/Construction waste—50%
20	Eco-pea coal
21	Eco-pea coal—90%/MDF *—10%
22	Eco-pea coal—50%/MDF—50%
23	Eco-pea coal—90%/RDF **—10%
24	Eco-pea coal—50%/RDF—50%
25	Eco-pea coal—90%/Textiles—10%
26	Eco-pea coal—50%/Textiles—50%
27	Eco-pea coal—90%/Waste paper—10%
28	Eco-pea coal—50%/Waste paper—50%
29	Eco-pea coal—90%/Plastic materials—10%
30	Eco-pea coal—50%/Plastic materials—50%
31	Eco-pea coal—90%/Rubber—10%
32	Eco-pea coal—50%/Rubber—50%
33	Eco-pea coal—90%/Multimaterial packaging—10%
34	Eco-pea coal—50%/Multimaterial packaging—50%
35	Eco-pea coal—90%/Diapers—10%
36	Eco-pea coal—50%/Diapers—50%
37	Eco-pea coal—90%/Construction waste—10%
38	Eco-pea coal—50%/Construction waste—50%
39	VARMO pellets
40	VARMO pellets—90%/MDF *—10%
41	VARMO pellets—50%/MDF—50%

Table 2. *Cont.*

Fuel Mixture Number	Fuel Mixture Composition
42	VARMO pellets—90%/RDF **—10%
43	VARMO pellets—50%/RDF—50%
44	VARMO pellets—90%/Textiles—10%
45	VARMO pellets—50%/Textiles—50%
46	VARMO pellets—90%/Waste paper—10%
47	VARMO pellets—50%/Waste paper—50%
48	VARMO pellets—90%/Plastic materials—10%
49	VARMO pellets—50%/Plastic materials—50%
50	VARMO pellets—90%/Rubber—10%
51	VARMO pellets—50%/Rubber—50%
52	VARMO pellets—90%/Multimaterial packaging—10%
53	VARMO pellets—50%/Multimaterial packaging—50%
54	VARMO pellets—90%/Diapers—10%
55	VARMO pellets—50%/Diapers—50%
56	VARMO pellets—90%/Construction waste—10%
57	VARMO pellets—50%/Construction waste—50%

* MDF—medium density fibreboard; ** RDF—refuse derived fuel.

Table 3. List of chemical elements determined in the ashes.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Measured parameter (ppm)	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Cu	Zn	Rb	Sr	Zr	Ba	Pb

The chemical elements determined in the ashes obtained from the mixtures of the basic fuels (wood pellets, eco-pea coal, and VARMO pellets) and the waste materials is presented in Table 3.

Figure 2 demonstrates colour maps representing the metal contents in the samples of ash after the combustion of pure wood pellets, eco-pea coal, and VARMO pellets, and the samples of ash obtained from the combustion of these fuels mixed with different waste materials (see Table 2). The colour map of the metal contents in samples of ash allows for clearly identifying the ash samples, which are characterised by the highest level of particular metal contamination.

It can be observed that the ashes originating from the combustion of pure wood pellets, eco-pea coal, or VARMO pellets demonstrated low contents of all the examined metals with the exception of parameters 16 and 17. In addition, the ashes from the combustion of all the pure fuels were characterised by the relatively highest contents of Sr and Zr (parameters 16 and 17) of all the examined ashes derived from the combustion of the mixtures of fuels and waste materials. It was found that the admixture of waste to the combustion process caused an increase in the content of the selected metals in the ashes. In the case of combusting wood pellets with the admixture of different waste materials (see Figure 2a), the highest concentration of phosphorus was noted for samples 4, 5, 7, 12, and 16–19.

Concerning samples 5, 10, and 13, the highest concentration of chlorine (parameter 7) of all the examined fuel mixtures was observed. Sample 9 was different from the remaining samples of wood pellets with the admixtures of waste materials because of its highest content of calcium (parameter 9). The highest contents of Mn, Rb, and Pb (parameters 11, 15, and 19) were observed for the ashes obtained from the combustion of samples 7, 3, and

10. Moreover, a very high content of Cu (parameter 13) was observed in the ash from the combustion of samples 6 and 14.

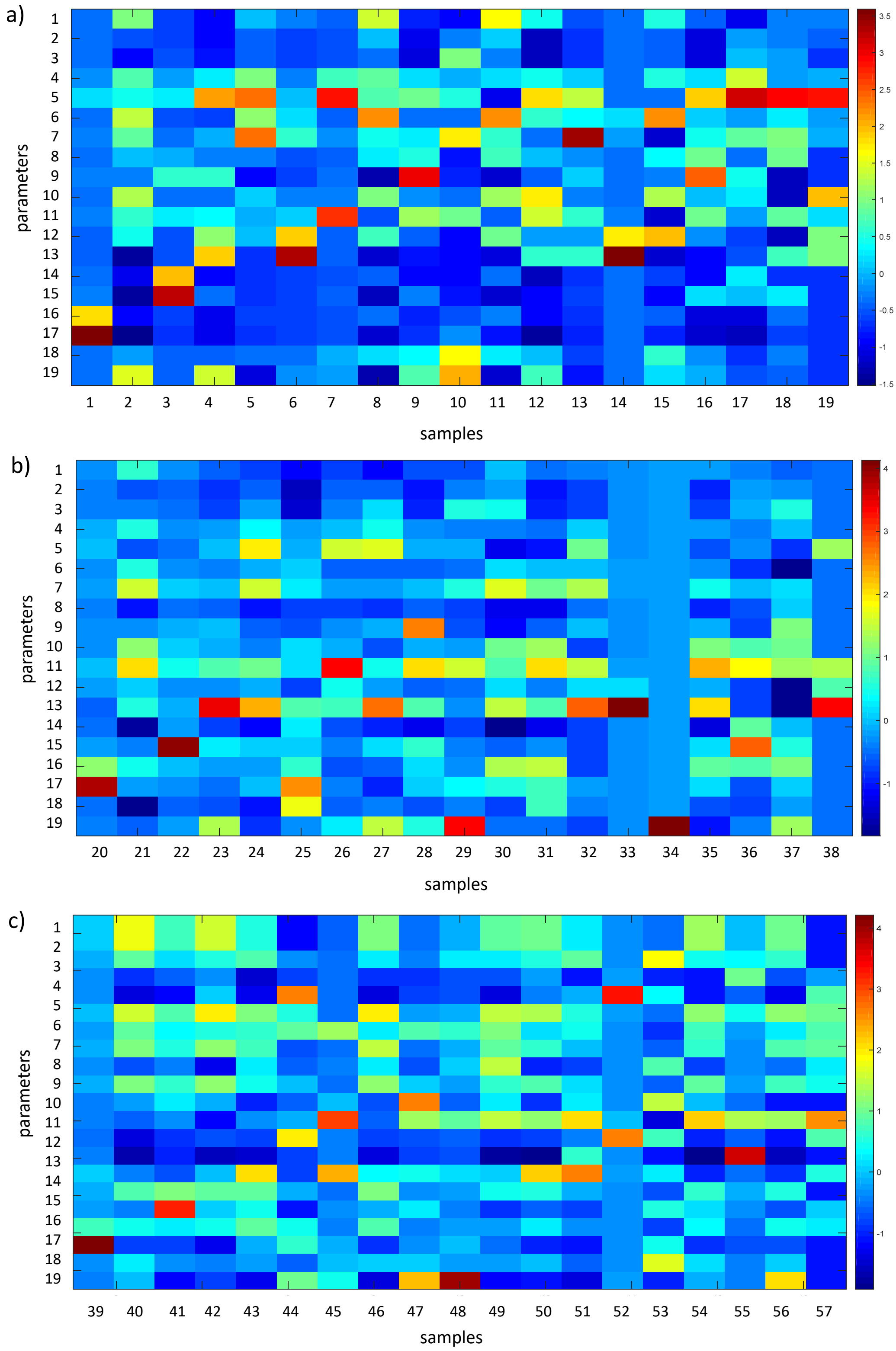

Figure 2. Colour map of the experimental data representing the metal contents in ashes after the combustion of (**a**) pure wood pellets, (**b**) eco-pea coal, and (**c**) VARMO pellets, and the ashes obtained from the combustion of these fuels mixed with different contaminants (see Table 2).

The analysis of the metal contents in the ashes after the combustion of mixtures of eco-pea coal (Figure 2b) and VARMO pellets (Figure 2c) with the admixture of waste was analogous. Based on the analysis of the results presented in Figure 2b, the highest contents of phosphorus in the ash (parameter 5) were observed for samples 24, 26, 27, 32, and 38. Additionally, high contents of chlorine were observed for samples 21, 24, 30, and 32. Particularly evident is the increase in the content of Mn and Cu (parameters 11 and 13) in the ash after the admixture of waste to eco-pea coal. In the case of Mn content, it is especially noticeable for samples 21, 26, 28, 29, 31, 32, and 35–38. As for parameter 13 (the content of Cu), the highest values were observed for samples 23, 24, 27, 32, 33, 35, and 38.

Furthermore, it can be seen that sample 22 was characterised by the highest content of Rb (parameter 15) of all the examined mixtures of eco-pea coal and waste. In turn, samples 23, 27, and 29 and 34 in particular were characterised by the highest content of Pb (parameter 19). Based on analysis of Figure 2c, it was found that the samples of VARMO pellets mixed with the waste materials were characterised by relatively higher contents of phosphorus, sulphur, and chlorine (parameters 5–7) in comparison with the ash samples obtained from the combustion of pure VARMO fuel.

In addition, samples 41, 45, and 55 were characterised by the highest contents of Rb, Mn, and Cu (parameters 15, 11, and 13) of all the examined VARMO mixtures. It was also observed that samples 47 and 48 differed because of the highest contents of Pb (parameter 19).

The application of the colour map of the experimental data enables identification of the similarities and differences among the examined ashes obtained from the combustion of pure fuels and the fuels with the admixtures of waste materials. Unfortunately, this simple analysis does not indicate the markers (metals) explicitly, and, in consequence, does not provide the answer if waste has been co-combusted in a given boiler. Therefore, based on the results of the measurements of the 19 chemical elements occurring in the post-combustion waste, building a model was attempted to facilitate the classification of the objects (the combusted samples of fuels with different admixtures of waste materials) into two groups of relevant levels of the contaminant contents. The general characteristics of the objects are presented in Table 4.

Table 4. General characteristics of the examined objects (combusted samples of fuels with different admixtures of waste materials).

Group Number	Fuel Content in the Sample (%)	Waste Material Content in the Sample (%)	Group Population
1(0)	90	10	27
2(1)	50	50	30

The discriminant analysis statistical tool was applied to build a model indicating the features (variables), which in a possibly optimal way would classify the examined objects (samples) into the groups shown in Table 4. In this research study, the chemical elements determined in the ash samples (see Table 3) constituted these features (variables). Concerning the analysed objects (ash samples), it was indicated which discriminant variables were decisive in allocating the objects to the group of ashes obtained from the combustion of the fuel with a smaller (90/10—group 1(0)) or a larger (50/50—group 2(1)) share of the waste materials. The calculations were performed using Statistica software. In the first phase of the statistical model design, it was determined which of the variables constitute the best discriminants (predictors). On this basis, the second phase consisted in validating the discrimination performed on the first set of objects by means of classifying the novel objects. In the designed model, the variables were (a) the dependent (grouping) variable of a qualitative and dichotomous character constituting the percentage share of waste in the examined object (sample): $Y = \begin{cases} 0 & 10\% \\ 1 & 50\% \end{cases}$ waste admixture in the fuel; and (b) the independent variables, from the set of which the discriminant variables were selected.

The set of the potentially discriminant variables included 19 chemical elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Zr, Ba, and Pb) whose contents in the examined objects (samples of fuels blended with the waste materials) was determined using X-ray fluorescence spectroscopy (XRF). The 57 objects (combusted samples of fuels with different admixtures of waste materials) were divided into two subsets, the training sample and the test sample.

3.1. Design of the Model Using a Training Sample

Table 5 presents the populations of the particular groups used to select the discriminant variables.

Table 5. Description of the sample used to build the so-called learning model.

Group Number	Fuel Content in the Sample (%)	Waste Material Content in the Sample (%)	Group Population
1(0)	90	10	15
2(1)	50	50	15

The model determining the variables, which in a possibly optimal way would classify the examined ash samples into the groups, was built by applying the training set described in Table 5 and using the Statistica software. The results of the discriminant analysis of the initial set of 19 variables are presented in Table 6.

Table 6. Results of the discriminant analysis for the training sample.

$n = 30$	Wilks' Lambda	Partial Wilks' Lambda	F Removed. (1,34)	p-Value	Tolerance	1-Tolerance (R^2)
K	0.7417	0.5078	23.262	0.0001	0.2144	0.7856
Ca	0.4973	0.7573	7.690	0.0106	0.6815	0.3185
Ti	0.7560	0.4982	24.175	0.0001	0.3561	0.6439
Zn	0.5333	0.7063	9.981	0.0042	0.6547	0.3453
Rb	0.4470	0.8427	4.480	0.0449	0.4868	0.5132

The value of the Wilks' lambda (λ) coefficient is within the range $[0; 1]$. The lower the value of coefficient λ, the greater is the contribution of a given variable to the discrimination of a set of the objects.

In the final model used for the discrimination, five variables were taken into consideration: K, Ca, Ti, Zn, and Rb. All of the variables revealed significant discriminant power as the calculated values of F-statistics and the corresponding values of p-value were lower than the assumed level of statistical significance $\alpha = 0.05$. Within the course of further analysis, the discriminant power of the estimated discriminant function was examined and a canonical analysis was performed, the results of which are given in Table 7.

Table 7. Results of canonical analysis for the training sample.

Removed	Own Value	Canonical R Value	Wilks' Lambda	χ^2	DF	p-Value
0	1.6550	0.7895	0.3767	24.8994	5	0.0002

Source: own, based on Statistica software (StatSoft, Tulsa, OK, USA).

The low value of Wilks' lambda coefficient, 0.3767 (see Table 7), indicates great discriminant power of the model described by the variables compiled in Table 6. All of the variables in Table 6 achieved the status of discriminant values in the model due to the fact that the calculated value of $\chi^2 = 24.8994$ and the corresponding p-value are lower than the assumed level of statistical significance $\alpha = 0.05$.

Equation (1) describes the discriminant function and includes raw coefficients of the estimated canonical function of discrimination:

$$d_i = 0.8789 + 2.4640 \cdot K - 0.0883 \cdot Ca - 2.6647 \cdot Ti - 0.315 \cdot Zn - 93.9848 \cdot Rb \quad (1)$$

In the next step, the coefficients of two classification functions for the tested objects in the training sample were calculated, given by Equations (2) and (3):

$$k_{1i} = -1.7079 + 2.1445 \cdot K + 0.0220 \cdot Ca - 0.7925 \cdot Ti + 0.0035 \cdot Zn - 22.3379 \cdot Rb \quad (2)$$

$$k_{2i} = -3.8927 - 3.9803 \cdot K + 0.2415 \cdot Ca + 5.8312 \cdot Ti + 0.7882 \cdot Zn + 211.2796 \cdot Rb \quad (3)$$

Then, based on the values obtained from the linear classifying functions, the objects from the training sample were allocated to one of the two groups. The results of the classification are presented in Table 8.

Table 8. Classification matrix constructed for the training sample.

	Percent Correct	**Group 1(0)**	**Group 2(1)**
Group 1(0)	100%	15	0
Group 2(1)	80%	3	12
Total	90%	18	12

The classification analysis of the objects (ash samples) in the training sample presented in Table 8 demonstrates 90% accuracy of group allocation. Only three samples, i.e., 20% of group 2(1), were falsely classified. Therefore, it is possible to state that the constructed model performs the classification task on the training sample correctly because the accuracy was as much as 90%.

The discriminatory model shown in Tables 6 and 7 reveals a good fit to the data used for its construction. However, the more important feature of the model is the actual predictive power of discrimination. Hence, it is necessary to check how the constructed model handles the classification of objects (the combusted fuel samples with different admixtures of waste materials) outside the training sample consisting of 30 objects (see Table 5). Data concerning the test sample for the validation of the classifying capability of the constructed discrimination model are presented in Table 9.

Table 9. Description of test sample used to validate the constructed model.

Group Number	**Fuel Content in the Sample (%)**	**Waste Material Content in the Sample (%)**	**Group Population**
1(0)	90	10	12
2(1)	50	50	15

3.2. Validation of the Constructed Model on Test Sample

The discrimination model built for the training sample was validated by means of classifying the data of the test sample. The allocation of the examined objects to the training and test samples was conducted according to the sequence of their combustion. The results concerning the prediction accuracy (classification) for the test sample are presented in Table 10.

Table 10. Results of the classification for the test sample.

	Percent Correct	Group 1(0)	Group 2(1)
Group 1(0)	83.33%	10	2
Group 2(1)	86.67%	2	13
Total	85.19%	12	15

Comparing the results of the classification for the training sample (see Table 7) with the results for the test sample (see Table 10), it was observed that there was a slight decrease in the percentage of the total correct classifications. The classification accuracy for the test sample for the discrimination model obtained for the training sample was 85.19%. This is likely caused by the small population of the test sample. However, the primary objective of this research study was to demonstrate the possibility of applying the discriminant analysis to unambiguously determine the chemical elements (variables), and, in consequence, to be able to assess into which group the object (actual ash sample coming from the combustion of the basic fuel with the admixtures of different waste materials) can be classified.

Table 6 compiles the variables (chemical elements) that play the role of the discriminant variables in the model validated by means of the data presented in Table 7. This data set includes elements such as K, Ca, Ti, Zn, and Rb. As demonstrated, the particular value of Wilks' lambda λ provides the information concerning their discriminant abilities. The standardised coefficients of the canonical function of discrimination whose raw values were given in Equation (1) constitute supplementary information. These coefficients are interrelated in a similar way as the standardised coefficients of the linear regression function. The higher absolute value shows which of the variables became the best predicator (stronger discriminant variable than the remaining ones) to the analysed groups of objects (combusted samples of fuel with the admixtures of waste material). Table 11 presents the discriminant variables according to the discriminant power of the examined objects.

Table 11. Standardised canonical discriminant function coefficients.

Variable (Chemical Element)	K	Ti	Zn	Ca	Rb
Value of the standardised coefficient	1.9193	−1.5036	−0.84834	−0.7558	−0.7200

It was found that K, Ti, Zn, Ca, and Rb were the chemical elements (variables) which demonstrated the discriminant power of the group of ash samples in terms of the content of contaminants; but the first two revealed decidedly the greatest discriminant power.

4. Conclusions

- This study involved conducting systematic research on the combustion of fuel samples such as wood pellets, eco-pea coal, and VARMO pellets with different admixtures of waste materials (10 and 50%*w/w*). The tests were performed using a research stand equipped with a heating boiler of a nominal power of 18 kW.
- Significant differences in the content of the 19 examined chemical elements in the ashes were observed, depending on the quality of the combusted fuel.
- Based on the discriminant analysis, a statistical model was constructed to classify the ash samples obtained from the combustion of fuels with different admixtures of waste materials.
- Based on application of the discrimination function and two functions of classification, the objects from the training sample were allocated. A validation was performed on the test sample. Both the learning model and the test model demonstrated a good fit of the data to the model, and, more importantly, a good prediction power for the new samples from the test set.
- Using the standardised coefficients of the canonical function of discrimination in the last step of the statistical analysis, it was found that potassium, zinc, calcium, and

rubidium constitute the chemical elements that had the greatest discriminatory power to classify the examined objects into the following two groups: ashes coming from the combustion of the fuel with a smaller share (90/10—group 1(0)) of waste materials and with a larger share (50/50—group 2(1)) of waste materials.

- On the basis of examining the elemental content of ashes, the empirical tests using the statistical discriminant analysis show the usability of the constructed model to identify the combustion of waste.

Author Contributions: Conceptualisation, K.W., J.G. and A.S.; methodology, K.W. and J.G.; formal analysis, K.W., J.G. and A.S.; investigation, K.W., J.G. and A.S.; data curation, K.W.; writing—original draft preparation, K.W. and J.G.; writing—review and editing, A.S.; visualisation, K.W.; supervision, A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science and Higher Education, Poland (grant number 11152019-335).

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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