1	Method for indication of municipal waste combustion in households by ash analysis
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8	
9	Abstract
10	The practice of co-combustion of municipal waste in domestic small-scale combustion units is
11	not only a problem of the Czech Republic. One way to prove that waste was burned in the
12	domestic combustion unit is to analyze residues after incineration - ash. The aim of this study
13	was to propose the method for indication of municipal waste combustion in households by ash

analysis. 73 samples of ash were obtained from the combustion of different solid fuels (such as spruce wood, beech wood, wood pellets, lignite, lignite briquettes, black coal and Flot coal slurries), their mixtures with municipal waste (floor coverings, paper, PET briquettes, plastics and textile) and municipal wood waste (furniture chipboard and window frames) in household combustion units. The limit values of the parameters were determined for metals Sb, Cu, Pb, Sn, Zn, Ti and chlorides in our previous study (Horák et al. 2019). The method called Semafor (English translation: traffic light) is based on three criteria: i) proof of municipal waste combustion (proven), ii) combustion of municipal waste cannot be proven or excluded (suspected) and iii) no proof of municipal waste combustion (not proven). The aim of further study is to confirm the application of proposed method and to extend the available analyses in case of not unequivocally proved combustion of municipal waste such as plastics.

26 Keywords: solid fuel; municipal waste; combustion; ash; households

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#### 28 Introduction

29 To author's knowledge, there are currently several methodologies for identifying waste30 combustion in domestic combustion units:

# 31 Swiss method (Umweltfachstellen 2015)

32 This methodology is proposed for proving the incineration of foreign admixtures with wood. 33 The sampled ash is first visually inspected in the laboratory by separating through a sieve, 34 finding "suspicious" residues, such as nails, screws, plastics, or aluminum foil, which is the 35 reason for filling a complaint, and the sample is no longer analyzed analytically. Visually 36 unobjectionable samples are judged from the point of view of the concentration of the 37 elements: chromium, copper, lead, zinc and chlorine. From these five elements (Table 1), the 38 percentage of the assessed value is calculated and added to the sum of the parameter. If the 39 sum of the percentages of all elements is more than 500% and at least two elements lie above 40 the assessed value, the ash sample is found to be contaminated by municipal waste.

41 Table 1. Limit values of indicators (mg/kg<sub>dry matter</sub>) published in (Umweltfachstellen 2015).

Limit values of indicators [mg/kg <sub>dry matter</sub> ]	Cr	Cu	Pb	Zn	Cl
EMPA 2001 (Swiss method)	100	150	100	600	2,000
ZUDK 2008 (Swiss method)	150	400	100	800	2,000
ZUDK 2010 (Swiss method)	150	600	100	1,500	2,000

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# 44 German standard (VDI 2016)

The content of firebox and firebox ash shall be visually inspected for the presence of foreign matter such as metallic residues (e.g. nails, screws) or plastics, textile, cardboard and paper scraps. If there are indications of unallowable fuels being used, this can be inspected by analyzing a composite sample of firebox residues. The reference values of heavy metals such as As, Pb, Cd, Cr, Cu, Ni, Zn, Cl and Ti are given in Table 2. They may be used for the 50 further assessment in the case of installations exclusively authorized for the operation of 51 untreated wood.

52 Table 2. Reference values for pollutant concentrations of ash from the combustion of 53 untreated wood in small firing installations (mg/kg<sub>dry matter</sub>) published in the standard (VDI 54 2016).

Reference values for ash pollutant concentrations in mg/kg								
arsenic (As)	lead (Pb)	cadmium (Cd)	chromium (Cr)	copper (Cu)	nickel (Ni)	zinc (Zn)	chlorine (Cl)	titanium (Ti)
30	200	10	400	600	200	2000	2000	1000

55

## 56

### 57 IChPW method (IChPW 2017)

It is a methodology of the IChPW Research Institute (Instytut Chemicznej Przeróbki Węgla), Zabrze, Poland. The ash is judged by the concentration of majority element oxides by a procedure that is non-public and copyrighted, but software prepared based on this method was transferred to the self-government units of the Silesian Voivodeship. The result of the evaluation is that i) waste incineration was excluded ("OK" designation), ii) waste incineration was confirmed ("NOK") or iii) waste incineration was not confirmed ("Confirm"). Due to the protected evaluation process, no limit values are available.

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# Method of the University of Krakow (Politechnika Krakowska im. Tadeusza Kościuszki), Poland

In the ash, Zn, Pb, Hg, Sb, Sn, Cu, Cr, Ni, Cd, organically bound nitrogen, phenols and
visually distinguishable plastics are analyzed and evaluated (Dragon 2015). The approach of
this method is not known by us as it is non-public.

72 New legislation has been adopted in the Czech Republic (369/2016 2016) in which is written 73 that the combustion of municipal waste in small-scale combustion units in households is forbidden. This paper refers to the method for indication of municipal waste combustion in 74 75 households by ash analysis published as Communication of the Ministry of the Environment of the Czech Republic (MoE 2018). The aim of our study was to elaborate the method for 76 77 determination of municipal waste combustion by ash analysis and to compare this method 78 with existing and published methods. The tool was the reference values of ash from the 79 combustion of solid fuels (biomass, lignite, black coal and unspecified fuel).

80

#### 81 Materials and methods

The detail description of used materials (solid fuels and municipal waste) and methods (combustion tests, methods of ash samples analysis) was published by Horák et al. (Horák et al. 2019). The description of 73 tests from the combustion tests performed in the Energy Research Center, Ostrava, Czech Republic and selected heavy metals Sb, Cu, Pb, Sn, Zn, Ti and chlorides are described in Table S1. The parameters were chosen according to analytical results and statistical evaluation summarized by Horák et al. (Horák et al. 2019).

88

# 89 **Results and discussion**

# 90 Assessment methods of ash analysis for the identification of waste incineration in domestic

91 *heating devices* 

The results of the analysis of selected ash samples from the combustion tests were evaluated by the methods described in Introduction and it was proved that the use of these methods is very limited for the conditions of the Czech Republic. The question of the applicability of the IChPW method, which needs to be validated for lignite from the Czech Republic, remains 96 open. These methods inspired the development of the final methodology for the indication of97 waste combustion by ash analysis.

98 The Swiss methodology was applied for 40 ash samples (Table S2). The methodology did not 99 prove the identification of combustion of paper, plastics, PET briquettes and partly furniture 100 chipboard.

German standard (VDI, 2016) does not show the methodology used for the evaluation of municipal waste combustion except of reference values for elements (Table 2). However, it can be expected that if the reference values are not exceeded, the municipal waste combustion was not proven (Table S3). The combustion of paper + dry beech and PET briquettes + dry beech was not proven.

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113

107 Proposal of waste incineration methodology by analysis of ash sample collected at the
108 operator

109 On the basis of the evaluation of the results, ash is indicated as: 1) ash from combustion of 110 municipal waste, 2) suspicious ash, 3) ash, which failed to prove the combustion of municipal 111 waste (which does not mean that the municipal waste was not burned, method did not prove 112 it).



Proof of municipal waste combustion = Proven

Combustion of municipal waste can not be proven or excluded = Suspicious

No proof of municipal waste combustion = Not proven

- 114 Fig. 1. The description of the applied method Semafor.
- 115 The assessment is made according to the type of declared fuel for 6 groups:
- biomass (e.g. wood, wood briquettes, wood pellets)

- 117 lignite and lignite briquettes
- 118 black coal
- 119 lignite + biomass
- 120 black coal + biomass
- 121 unspecified fuel
- 122

#### 123 Limit values of indicators

Limit values of indicators were set for each group of solid fuel. The calculation of the limit values was based on the analysis of ash from the combustion of solid fuels. The limit values of the indicators were determined for metals Sb, Cu, Pb, Sn, Zn, Ti and chlorides. It is assumed that for the indication of waste incineration it will be required to determine the concentration of Sb, Cu, Pb, Sn, Zn, and Cl<sup>-</sup> in the ash sample always, whereas the determination of the "Ti" concentration will be required only in case of combustion of biomass.

131 The limit values of the individual monitored indicators were calculated from the maximum 132 concentration of the particular substance in the results. Unusually, high concentrations 133 (suspicious maxima) were excluded from the calculation of the limit value or were left out in 134 the calculation on the basis of the examination (e.g. repeated analysis or assessment of 135 possible contamination of the ash sample). The maximum concentration value of the relevant indicator was then increased by 30% (assumed maximum uncertainty of the analysis in the 136 137 test laboratory) and rounded to the next highest divisible number of 5 for better clarity. This 138 value is marked as the limit. This procedure was performed for each indicator.

The maximum values of the individual indicators are shown in graphs, which are presented
separately for each group of declared fuels: biomass – Fig. S1, lignite and lignite briquettes –
Fig. S2, black coal– Fig. S3.

- 142 The resulting limit values of the individual indicators of the Semafor method are shown in
- 143 Table 4.

	Limit values of indicators [mg/kg <sub>dry matter</sub> ]	Sb	Cu	Pb	Sn	Ti	Zn	Cl
	Semafor (biomass)	10	390	55	10	1,835	3,070	1,690
	Semafor (lignite)	5	300	35	5	х	375	2,015
	Semafor (black coal)	10	130	75	10	х	145	1,690
	Semafor (lignite + biomass)	10	390	55	10	х	3,070	2,015
	Semafor (black coal + biomass)	10	390	75	10	х	3,070	1,690
145	Semafor (unspecified fuel)	10	390	75	10	х	3,070	2,015

144 Table 4. Limit values of indicators of the Semafor method (MoE 2018).

- 146
- 147 Calculation of exceedance index according to the equation:

148 exceedance index[%] = 
$$\frac{measured concentration of the indicator \left[\frac{mg}{kg_{dry matter}}\right]}{limit value of the indicator \left[\frac{mg}{kg_{dry matter}}\right]} \cdot 100$$

- 149 Criteria of assessment of particular indicator:
- Allowed value exceedance index of the indicator is lower or equal to 100%
- Significantly exceeded value exceedance index of the indicator is higher than 200%
- Suspicious value exceedance index of the indicator is higher than 100% and lower or
   equal to 200%.
- 154 Criteria of assessment of ash samples:
- 155 RED = Proof of municipal waste combustion

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    Two or more significantly exceeded value (minimally two exceedance indexes are
    higher than 200%)
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- 158 ORANGE = Combustion of municipal waste cannot be proven or excluded
- Two or more suspicious values (minimally two exceedance indexes are higher than
   100% and lower or equal to 200%) or one significantly exceeded value (one
   exceedance index is higher than 200%)
- 162 GREEN = No proof of municipal waste combustion

... .

- All allowed value (all exceedance indexes are lower or equal to 100%) or maximally
   one suspicious value (one exceedance index is higher than 100% and lower or equal to
   200%).
- 166 The proposed method was used to evaluate the ashes from the combustion of municipal waste
- 167 by the Semafor method, Tables 5 (28 samples) and Table S4 (73 samples).
- 168
- 169 Table 5. The evaluation of identification of municipal waste combustion by Semafor method.

Sample	Fuel	Semafor method		
1	furniture chipboard	proven		
3	textile + B1	proven		
5	textile + L2	proven		
8	window frames	proven		
9	floor covering $+$ B1	proven		
10	textile + dry beech	proven		
11	floor covering $+$ L1	proven		
12	floor covering + dry beech	proven		
13	paper + B1	not proven		
14	paper + dry beech	suspicious		
15	paper + L2	not proven		
16	PET briquettes + dry beech	suspicious		
17	PET briquettes + L2	suspicious		
18	plastics + dry beech	proven		
19	plastics + B1	suspicious		
20	plastics + dry beech	proven		
21	plastics $+$ L2	suspicious		
22	paper + dry beech	not proven		
23	plastics + dry beech	suspicious		
24	furniture chipboard	proven		
25	PET briquettes + dry beech	suspicious		
26	window frames	proven		
29	floor covering + dry beech	proven		
31	paper + dry beech	not proven		
33	textile + dry beech	proven		
35	window frames	proven		
46	furniture chipboard	suspicious		
73	furniture chipboard	proven		

171 The application of the method Semafor showed that red was 16 samples, orange was 8

172 samples and green was 4 samples (Table 6).

173

174 Table 6. The summary of applied Semafor method.

	green	orange	red
floor coverings	0	0	4
furniture chipboard	0	1	3
paper	4	1	0
PET briquettes	0	3	0
plastics	0	3	2
textile	0	0	4
window frames	0	0	3

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177 The proposed method could:

- clearly prove the combustion of floor coverings, textiles and window frames,
- very successfully prove the combustion of furniture chipboard,

• indicate the combustion of PET briquettes and plastics,

• not prove the combustion of paper.

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183 The comparison of Semafor method, Swiss method and German standard is shown in Table 184 S5. Swiss method and German standard were evaluated only for municipal waste combusted 185 with wood. From the results, it can be concluded: i) Semafor and Swiss methodologies clearly 186 prove the combustion of floor coverings, textiles and window frames, ii) the combustion of 187 furniture chipboard were successfully proven by Semafor and indicated by Swiss method (2 188 combustions were proven, 2 combustions were not proven); iii) the combustion of PET 189 briquettes and plastics were indicated by Semafor method, not proven by Swiss method and 190 German standard (herein, only PET briquettes evaluated); iv) the combustion of paper was not 191 proven by any of applied methods. To prove the combustion of PET briquettes and plastics

and paper, more combustion tests with the specification of the Semafor method will be theaim of further study.

194 The Semafor method was applied for solid fuels for which the method did not prove the195 combustion of contaminated fuels (Table S4).

196

#### 197 Conclusions

198 Total number of 73 ash samples were analyzed within the research on the identification of 199 combustion of unsuitable fuels in household boilers and stoves. There were 45 ash samples of 200 solid fuels and 28 ash samples of municipal waste. Samples of ash were obtained from the 201 combustion of seven solid fuels, their mixtures with municipal waste (five) and municipal 202 wood waste (two) in household combustion units. Limit values of seven indicators (Sb, Cu, 203 Pb, Sn, Zn, Ti and Cl<sup>-</sup>) were set for each group of solid fuel (biomass, lignite, black coal and 204 unspecified fuel). The new created method called Semafor was applied for 73 combustion 205 tests and compared with other methodologies. The Semafor method was applied for solid 206 fuels for which the method did not prove the combustion of contaminated fuels. Sixteen ash 207 samples from the combustion of municipal waste were proved, eight ash samples were 208 suspicious and four ash samples were not proved. The proposed Semafor method could: i) 209 clearly prove the combustion of floor coverings, textiles and window frames; ii) very 210 successfully prove the combustion of furniture chipboard; iii) indicate the combustion of PET 211 briquettes and plastics; and iv) not prove the combustion of paper.

212

#### 213 **Declarations**

214 Ethics approval and consent to participate: Not applicable.

215 Consent for publication: Not applicable.

- 216 Availability of data and materials: All analysed data during this study are included in this
- 217 published article and its supplementary information files.
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- 221 Original Draft, Visualization, MD: Methodology, Project administration, SB: Validation,
- 222 Investigation, FH: Writing Original Draft, Formal analysis, JK: Validation, Investigation,
- 223 KK: Methodology, JR: Formal analysis, OM: Visualization, MG: Resources.
- 224

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