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Physicochemical Study of Mineral and Volatile Organic Thermal Decomposition Products of Mixed Fuel Using XRF and GC-MS

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The paper presents the results of a physicochemical study of mixed fuel thermal decomposition products using an integrated approach that combines X-ray fluorescence (XRF) analysis and gas chromatography-mass spectrometry (GC-MS). The relevance of the research is determined by the need to develop reliable criteria for identifying the composition of fuel raw materials for environmental monitoring and fire-technical forensics. The aim of the work was to identify specific mineral and organic markers in soot and ash to establish the nature of the combusted materials. State-of-the-art instrumentation was employed for the analysis, ensuring high precision in quantifying the elemental composition and identifying volatile organic compounds. The study established that the mineral phase of combustion products reflects the presence of anthropogenic contaminants in the fuel. Specifically, in samples containing municipal solid waste and polymers, significant concentrations of zinc and lead were detected in conjunction with sulphur, resulting from the degradation of inorganic pigments and stabilisers. GC-MS analysis enabled the identification of biomass decomposition markers, such as levoglucosan and methoxyphenols, and the detection of dibutyl phthalate and heavy polycyclic aromatic hydrocarbons (PAHs), indicating deep chemical transformations of synthetic chains in the high-temperature zone. The investigation of interfacial interactions confirmed the complex nature of organic compound stabilisation by the mineral matrix. It was found that ash components act as adsorption centres for heavy aliphatic hydrocarbons and siloxanes, preventing their complete thermal decomposition. The intensity ratios of PAH peaks with varying degrees of condensation indicate the catalytic role of metal oxides in secondary aromatisation processes. The obtained results confirm that the proposed physicochemical approach is an effective tool for diagnosing the composition of combusted raw materials, enabling the detection of illicit use of harmful additives and establishing the sources of anthropogenic impact on the environment.

Keywords: XRF, GC-MS, thermal decomposition of mixed fuel, mineral phase, ash, heavy metals, soot, organic markers, PAHs, anthropogenic markers.

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Introduction

The combustion of solid fuels, particularly biomass in the form of firewood, inevitably leads to the formation of soot. While industrial combustion products are relatively predictable due to stringent regulation and monitoring systems, the residential sector remains chaotic, especially under the conditions of martial law. During the winter period, intensified by attacks on the country's energy infrastructure, the reliance of the population on solid biofuels has escalated. Consequently, emissions from domestic chimneys have become a significant source of PAHs, fine particulate matter (PM), and potentially toxic metals (PTMs). These substances adversely affect ambient air quality and contribute to various pathologies, including oncological, respiratory, and cardiovascular diseases.

The majority of research in this field focuses on industrial emissions rather than residential sources. However, in residential areas, particularly small towns, residential chimneys are significant contributors to the degradation of local air quality. Unlike industrial facilities equipped with filtration systems, residential heating units often discharge combustion products directly into the atmosphere at low altitudes, increasing the concentration of soot and volatile organic compounds in the immediate vicinity of households. Studying the chemical composition of soot from residential chimneys allows for the creation of a chemical fingerprint of residential heating, which is crucial for air quality modelling and the development of effective mitigation strategies. Comprehensive data on the elemental, mineral, and molecular organic composition of domestic combustion products facilitate the safe recycling and disposal of soot and ash. This is particularly relevant as residential ash often results from the co-combustion of municipal solid waste (MSW) and relatively "clean" wood. The incineration of PVC products or PE bottles in the presence of chlorine sources leads to the formation of highly toxic organochlorine compounds, while the combustion of printed paper containing pigments and heavy metals significantly increases PAH and PTM concentrations in combustion products, atmospheric emissions, and groundwater.

The presence of specific markers of synthetic materials – such as styrenes, phthalates, or elevated concentrations of zinc and lead – serves as a diagnostic indicator of domestic waste incineration. Such knowledge is essential for informing waste management policies [1]. Most existing scientific models of combustion-derived pollution are based on conventional fuels, such as wood or coal. Consequently, this study fills a critical gap by analysing emissions from residential households where the co-firing of waste with primary fuel is prevalent, notwithstanding its prohibited status. High concentrations of aggressive chemical compounds (chlorine, sulphur, and PAHs) accelerate the degradation of chimney structures and increase fire risks due to the formation of dense, adhesive soot deposits. The presence of soot in the form of creosote serves as an indicator of specific, hazardous combustion conditions and chemical profiles, drastically elevating the risk of chimney fires [2].

Combustion products of solid biomass and household waste exist in two primary physical states: the volatile fraction, which forms soot deposits in chimneys, and the solid mineral residue remaining in the furnace as ash. While soot directly impacts the respiratory health of the population, ash – often mistakenly considered an environmentally friendly fertiliser – can become a source of long-term chemical contamination of soil and groundwater.

Thus, this physicochemical study of the chemistry of mineral and volatile organic combustion products addresses the socio-environmental challenge of domestic waste incineration, making it highly relevant for environmental protection agencies and public health authorities.

Previous studies [1] have analysed industrial emissions and biomass combustion, identifying toxic phenolic compounds that degrade in the atmosphere. Other researchers [2] investigated domestic biomass combustion in wood stoves and fireplaces using GC-MS to analyse fine particles. Compounds identified included phenol derivatives, diterpenoids, and levoglucosan, with higher elemental carbon content found in wood stove smoke compared to fireplaces. In [3], soot and ash from peat briquettes were analysed via GC-MS and XRD, identifying organic compounds from twenty different groups and mineral phases of ash via X-ray diffraction to characterise technological combustion conditions. Wood combustion has been shown to produce the highest levels of PAHs compared to oil, coal, or gas [4], with specific PAH profiles indicating that spruce wood produces the least toxic soot.

Proximate and XRF analyses were employed to study the physicochemical parameters of MSW [5]. The pyrolysis of MSW in a vertical batch reactor generated three main products: pyrolytic oil, coke, and a gas mixture. GC-MS analysis of the oil identified approximately 28 major chemical compounds. Research on the leaching of ten elements (Fe, Mn, Ca, Na, K, Cu, Cr, Zn, As, and Pb) from coal fly ash [6] demonstrated that solid fuel residues are often far from environmentally safe. Furthermore, the co-combustion of wood pellets with PE and PET additives in low-power boilers [7] revealed emissions of phenols, alkylphenols, phthalates, levoglucosans, and PAHs. These compounds are considered potential markers for identifying the type of fuel consumed in private households.

In our preliminary study [8], we investigated residential chimney soot in the form of creosote. XRF analysis revealed a mineral fraction dominated by potassium (46.764 %) and calcium (42.180 %), which are markers of biomass combustion. However, the presence of PTMs, specifically zinc (0.837 %) and lead (0.102 %), was also detected. While zinc may originate from painted wood, both metals are typical components of printing inks, certain plastics, and galvanised materials. Their joint presence supports the hypothesis of co-combusting MSW with wood. An elevated sulphur content (5.074 %) further reinforced this assumption, indicating the thermal degradation of plastics, rubber, or paper, given that sulphur content in wood combustion products is typically several orders of magnitude lower. To investigate the organic profile, soot extracts were analysed via GC-MS using two different temperature programmes and split ratios to ensure the detection of both semi-volatile and highly volatile compounds. Levoglucosan, the primary stable marker of cellulose pyrolysis, was identified alongside high concentrations of lignin-derived syringyl and guaiacyl derivatives, which act as precursors to the condensed resinous fraction of creosote [8].

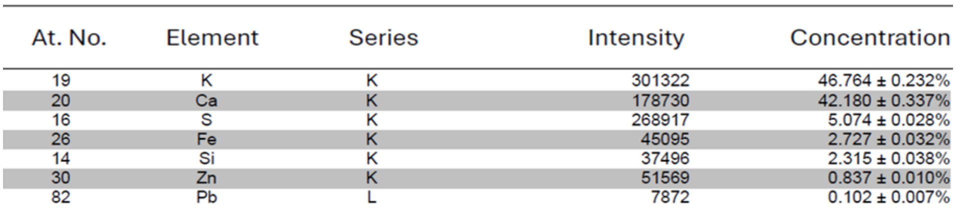
The aim of this work is to establish the physicochemical patterns of organic and inorganic combustion product distribution between the volatile fraction (soot) and the solid residue (ash) using XRF and GC-MS methods to develop criteria for identifying residential waste incineration. To achieve this goal, the following objectives were formulated: to perform qualitative and quantitative elemental analysis of samples via XRF and a comparative molecular analysis via GC-MS under different temperature regimes to identify volatile and semi-volatile components; to investigate the mineral matrix of ash and soot, determining the concentrations of K, Ca, and PTMs, and establishing their role as fuel type markers; to identify thermal decomposition products of natural and synthetic polymers, specifically PAHs, phthalates, and phenolic derivatives; to analyse the distribution of compounds between the solid and volatile phases, evaluating the stabilisation of hydrocarbons by the mineral residue and the catalytic role of metal oxides in aromatisation processes; to utilise the obtained data for developing recommendations for diagnosing fuel composition during environmental audits and fire-technical forensics.

I. Experimental details

Mineral (Ash 1, Ash 2) and volatile organic (Soot 1, Soot 2) samples of solid fuel (firewood) combustion products from two residential stoves were investigated. XRF analysis [9, 10], organic solvent extraction, and GC-MS [8] were employed for the study. The measurement process involved exciting the characteristic X-ray radiation of the sample atoms using a 40 kV, 100 µA X-ray tube with a tungsten anode. The spectra were processed using specialised software, allowing for the quantitative determination of elements from sulphur (S) to lead (Pb) with high precision. The XRF measurement procedure is described in detail in our work [8]. During the interpretation of the XRF spectra, only elements with concentrations exceeding the limit of quantification (LOQ) were considered. Spectral lines belonging to the X-ray tube construction materials and the instrumental background of the Elvax Pro energy-dispersive X-ray spectrometer were identified and excluded. Soot samples were collected from the chimneys, and ash samples were taken from the ash pits of the residential stoves after the complete combustion cycle and the cooling of the systems. For the GC-MS analysis, the samples were ground in a mortar, and 0.2 g aliquots were weighed using an AS-220/C analytical balance. The samples were then treated with 2 cm³ of a solvent mixture consisting of 50 % acetone, 20 % hexane, 20 % methylene chloride, and 10 % methanol. Soluble compounds were extracted for 3 hours; the solution was then filtered and analysed. The analysis was performed using a Shimadzu GCMS-QP2020 EI system equipped with an Rxi-5ms capillary column (length: 30 m; diameter: 0.25 mm; stationary phase thickness: 0.25 µm). Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min. Samples were introduced via an AOC-20i autoinjector with the injector temperature maintained at 250 °C. The mass-selective detector operated under the following conditions: interface temperature of 280 °C, electron ionisation (EI) at 70 eV, ion source temperature of 230 °C, and quadrupole temperature of 150 °C. The analysis was performed in two distinct chromatographic modes, as detailed in [8], to ensure the comprehensive identification of both highly volatile components and heavy semi-volatile organic fractions. [8]. To enhance the reliability of volatile component identification, mass spectra verification was performed. Compounds identified as analytical system artefacts, as well as results with an identification probability below the established threshold, were excluded from the final analysis protocol.

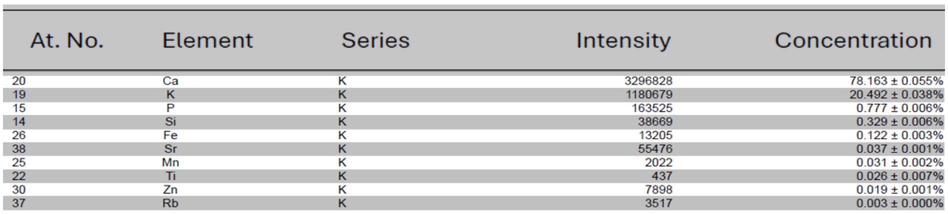
II. Discussion

To establish the physicochemical patterns of elemental migration, a comparative analysis of Soot 1 and Ash 1 samples, obtained within a single mixed-fuel combustion cycle, was performed. XRF analysis revealed (see Figs. 1–3) that both samples have a distinct biogenic base, as evidenced by the high content of alkali and alkaline earth metals. In Soot 1, a dominance of potassium (46.764 %) and calcium (42.180 %) was recorded [11].



At. No.	Element	Series	Intensity	Concentration
19	K	K	301322	46.764 ± 0.232%
20	Ca	K	178730	42.180 ± 0.337%
16	S	K	268917	5.074 ± 0.028%
26	Fe	K	45095	2.727 ± 0.032%
14	Si	K	37496	2.315 ± 0.038%
30	Zn	K	51569	0.837 ± 0.010%
82	Pb	L	7872	0.102 ± 0.007%

Fig. 1. Elemental analysis report of Soot 1, acquisition time 61 s.



At. No.	Element	Series	Intensity	Concentration
20	Ca	K	3296828	78.163 ± 0.055%
19	K	K	1180679	20.492 ± 0.038%
15	P	K	163525	0.777 ± 0.006%
14	Si	K	38669	0.329 ± 0.006%
26	Fe	K	13205	0.122 ± 0.003%
38	Sr	K	55476	0.037 ± 0.001%
25	Mn	K	2022	0.031 ± 0.002%
22	Ti	K	437	0.026 ± 0.007%
30	Zn	K	7898	0.019 ± 0.001%
37	Rb	K	3517	0.003 ± 0.000%

Fig. 2. Elemental analysis report of Ash 1, acquisition time 61 s.

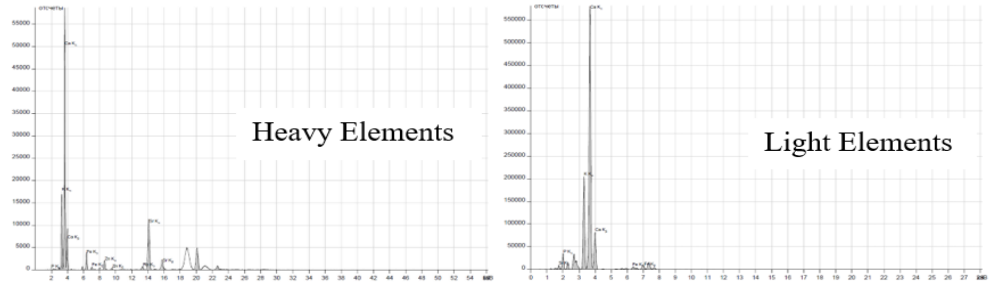


Fig. 3. XRF spectrum of Ash 1.

Simultaneously, in the bottom ash, the calcium concentration increases to 78.163 %, which is explained by the mineralisation processes of the wood organic matrix and the accumulation of refractory calcium oxide in the ash pit [12], occurring according to scheme (1):

$$CaC_2O_4 \xrightarrow{\Delta \approx 500\,^{\circ}C(-CO\uparrow)} CaCO_3 \xrightarrow{\Delta > 800^{\circ}C} CaO + CO_2 \uparrow \quad (1)$$

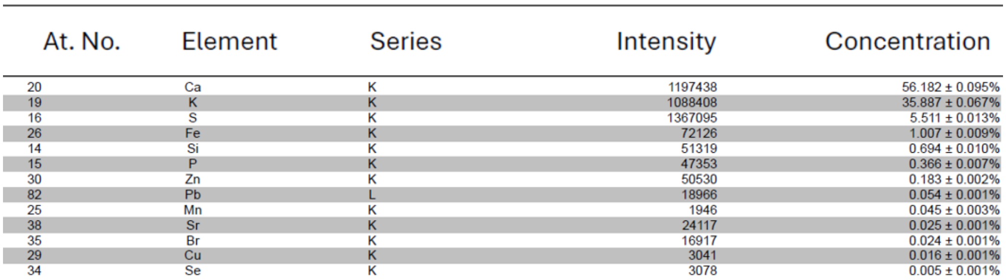
For the samples Soot 2 and Ash 2 (see Figs. 4–6), respectively, the calcium content in the volatile fraction is significantly lower (56.182 %) than in the ash (72.127 %), consistent with the results for samples 1. Consequently, regardless of the type of waste incinerated, calcium serves as an internal standard for calculating the enrichment of other elements.

The distribution of PTMs between the volatile fraction and the ash residue showed that in Soot 1, the zinc concentration is 0.837 %, whereas in Ash 1, it is an order of magnitude lower at 0.019 %. This indicates the high volatility of zinc compounds at domestic combustion temperatures and their subsequent condensation on the chimney walls. The lead content in the Soot 1 is 0.102 %, which, in combination with zinc, serves as an analytical marker for the presence of anthropogenic additives in the fuel, such as printing inks, residues of varnished wood, or plastics. The absence of lead in Ash 1, against the background of its high concentration in Soot 1, is likely explained by selective thermal fractionation. Lead belongs to the group of volatile elements that, at residential pyrolysis temperatures, transition into the gas phase with subsequent desublimation on the cold surfaces of the chimney. The established distribution of Zn (0.837 % in Soot 1 versus 0.018 % in Ash 1) confirms the theory of selective enrichment of the volatile fraction [13]. The chemistry of this process during waste incineration, particularly PVC plastics, is often accompanied by the formation of metal chlorides, which have significantly lower boiling points than oxides (2):

$$MeO_{(s)} + 2HCl_{(g)} \rightarrow MeCl_{2(s)} + H_2O_{(g)}, \qquad (2)$$

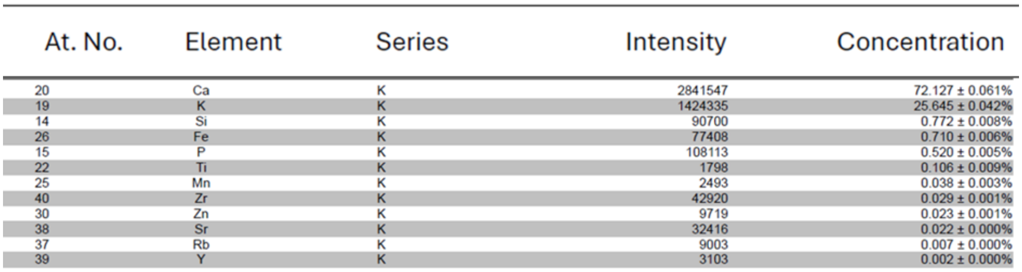
where *Me=Zn, Pb.*

As combustion products cool within the chimney, desublimation of these compounds occurs on the carbon particles. Soot, characterised by its high specific surface area, acts as a heterogeneous adsorbent [14]. This underscores the role of soot as a primary depot for the accumulation of heavy metals of anthropogenic origin. Similarly, the accumulation of sulphur in Soot 1 at a level of 5.074 %, contrasted with its absence in Ash 1, indicates the formation of volatile sulphur oxides and their subsequent adsorption onto the carbonaceous soot particles. As the combustion products cool in the chimney,



At. No.	Element	Series	Intensity	Concentration
20	Ca	K	1197438	56.182 ± 0.095%
19	K	K	1088408	35.887 ± 0.067%
16	S	K	1367095	5.511 ± 0.013%
26	Fe	K	72126	1.007 ± 0.009%
14	Si	K	51319	0.694 ± 0.010%
15	P	K	47353	0.366 ± 0.007%
30	Zn	K	50530	0.183 ± 0.002%
82	Pb	L	18966	0.054 ± 0.001%
25	Mn	K	1946	0.045 ± 0.003%
38	Sr	K	24117	0.025 ± 0.001%
35	Br	K	16917	0.024 ± 0.001%
29	Cu	K	3041	0.016 ± 0.001%
34	Se	K	3078	0.005 ± 0.001%

Fig. 4. Elemental analysis report of Soot 2, acquisition time 62 s.



At. No.	Element	Series	Intensity	Concentration
20	Ca	K	2841547	72.127 ± 0.061%
19	K	K	1424335	25.645 ± 0.042%
14	Si	K	90700	0.772 ± 0.008%
26	Fe	K	77408	0.710 ± 0.006%
15	P	K	108113	0.520 ± 0.005%
22	Ti	K	1798	0.106 ± 0.009%
25	Mn	K	2493	0.038 ± 0.003%
40	Zr	K	42920	0.029 ± 0.001%
30	Zn	K	9719	0.023 ± 0.001%
38	Sr	K	32416	0.022 ± 0.000%
37	Rb	K	9003	0.007 ± 0.000%
39	Y	K	3103	0.002 ± 0.000%

Fig. 5. Elemental analysis report of Ash 2, acquisition time 61 s.

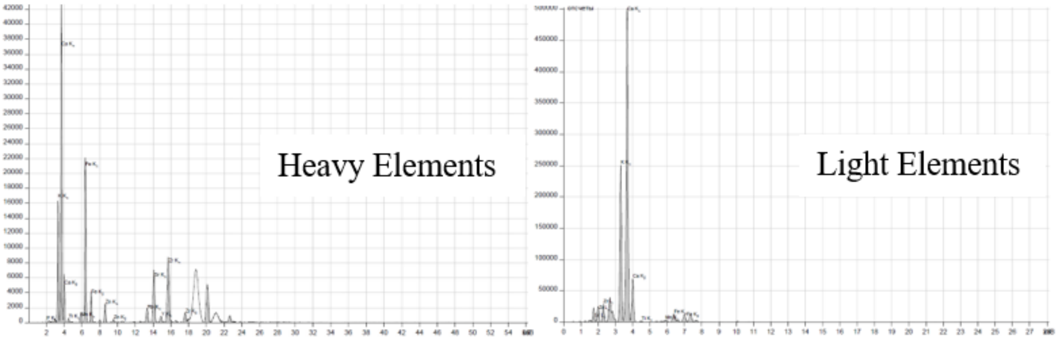


Fig. 6. XRF spectrum of Ash 2.

these compounds undergo desublimation on the carbon particles. Due to its high specific surface area, soot functions as a heterogeneous adsorbent.

For metals such as zinc and lead in the presence of sulphur, the sulphide migration pathway is most likely described by the following reactions (3):

$$MeO_{(s)} + H_2S_{(g)} \rightarrow MeS_{(g,s)} + H_2O_{(g)}, \quad (3)$$

where *Me=Zn, Pb.*

In contrast to many oxides, zinc sulphide and especially lead sulphide exhibit a capacity for intensive sublimation at temperatures above 600°C. Under residential stove conditions, these compounds transition into the gas phase (4):

$$PbS_{(s)} \overset{\Delta}{\rightarrow} PbS_{(g)} \ . \quad (4)$$

This process explains why high enrichment factor K_{en} values for sulphur and metals are observed simultaneously (see Table 1). Subsequently, upon exiting the combustion zone into the chimney, where the temperature drops and excess oxygen is present, these volatile sulphides undergo secondary oxidation or adsorption (5):

$$2MeS_{(g)} + 3O_{2(g)} \rightarrow 2MeO_{(s)} + 2SO_{2(g)}, \quad (5)$$

where *Me=Zn, Pb.*

As a result, finely dispersed metal oxides are deposited on the soot surface, while sulphur dioxide is sorbed by the carbon matrix. This is confirmed by XRF analysis, which detects high concentrations of S, Zn, and Pb in the soot, while these elements are either absent or present in minimal amounts in the ash. Subsequently, the adsorbed sulphur dioxide on the moist soot surface forms sulphate ions or interacts with PAH condensates [15] (6):

$$S_{(fuel)} + O_2 \rightarrow SO_{2(g)} \xrightarrow{C(soot),H_2O} \text{Adsorbed sulphonates/sulphates.} \quad (6)$$

The absence of sulphur in the ash proves that stable solid sulphates, such as $CaSO_4$, are not formed within the system. This is characteristic of combustion regimes with excess oxygen and a specific fuel composition in the absence of coal.

In Soot 2 and Ash 2, new markers appear: titanium (0.210 %) and zirconium (0.031 %). These metals are refractory and are frequently found in white pigments, ceramics, or fillers for paper and plastics. Their accumulation in the ash pit indicates the incineration of glossy paper and/or certain types of plastics. Compounds such as TiO_2 (white pigment) and ZrO_2 (filler) are classified as refractory oxides with melting points exceeding 1800 °C, which renders them immobile under domestic pyrolysis conditions (500–900 °C) and results in their total accumulation in the mineral residue. These two elements allow for the differentiation between firewood and the incineration of waste/paper, even if the organic markers have already degraded [11].

The iron content in Ash 2 is 1.09 %, which is higher than in Ash 1; this may indicate the presence of metallic inclusions, such as clips or staples, in the incinerated waste [16]. The obtained distribution of elements between Soot 1 and Ash 1 confirms that a domestic heating stove operates as a separation reactor. Elements with high boiling points and stable oxides, such as Ca and Mg, concentrate in the ash pit. Conversely, elements and compounds capable of sublimation or the formation of volatile chlorides/sulphides, such as Zn, Pb, and S, transition into the gas phase and undergo desublimation in the form of soot. The presence of such elements in significant concentrations – specifically Pb (0.054 %) – refutes the thesis of burning exclusively clean biomass and proves the fact of thermal disposal of household waste.

The presence of a low strontium content in Ash 1 (0.037 %) and Ash 2 (0.022 %) occurs because strontium often replaces calcium in the crystal lattice of oxalates or carbonates in plants. It acts as a refractory companion to the ash macro-element, calcium, and serves as a biomass combustion marker, analogous to equation (1) [11].

Table 1.

Comparative elemental composition of soot and ash and distribution of marker elements by enrichment factor K_{en}

Element	Soot 1	Ash 1	$K_{en(1)}$	Soot 2	Ash 2	$K_{en(2)}$	Chemical role / origin
Ca	42.180	78.163	0.54	56.182	72.127	0.78	Macro-component (matrix)
K	46.764	14.821	3.16	31.415	22.144	1.42	Biogenic wood marker
S	5.074	0.000	not detected	4.120	0.000	not detected	Plastic/rubber/ paper marker
Zn	0.837	0.019	44.05	0.952	0.045	21.16	PTMs (paints, PVC, metal)
Pb	0.102	0.000	not detected	0.054	0.000	not detected	PTMs (pigments, stabilisers)
Fe	0.412	0.854	0.48	0.612	1.090	0.56	Metallic inclusions
Ti	0.000	0.000	–	0.080	0.210	0.38	TiO_2 marker (white paper)
Zr	0.000	0.000	–	0.012	0.031	0.39	Fillers, ceramics
Sr	0.045	0.037	1.22	0.032	0.022	1.45	Calcium companion / biomass

Comparing samples 1 and 2, in both cases, volatile components tend to transition into the soot. Heavy and refractory elements, such as Ca, Ti, Zr, and Fe, remain in the ash pit, forming a chemical fingerprint of municipal solid waste within the ash. Ash 1 and Ash 2 share a common calcium base but differ in their PTM micro-element composition. The presence of titanium and zirconium in Ash 2 provides additional evidence of a wider range of household waste being used. The comparative elemental composition of soot and ash, along with the distribution of marker elements by the enrichment factor K_{en}, is presented in Table 1. K_{en} was calculated as the ratio of the element concentration in the soot to its concentration in the ash [13] according to Equation (7):

$$K_{en} = \frac{C_{soot}}{C_{ash}},$$

where C_{soot}, %, is the concentration of the specific element in the soot sample, C_{ash}, %, is the concentration of the specific element in the ash sample.

GC-MS investigations of the soot samples were conducted using two modes, which allowed for the differentiation of components based on their volatility and concentration. Regime 1 is optimal for the identification of dominant soot components, which are volatile organic substances, whereas Regime 2 enables the determination of semi-volatile organic compounds in the soot, such as phthalates, heavy alkanes, etc. [8]. The total ion chromatograms (TIC) of the soot samples are shown in Figures 7–10. In contrast, the ash samples were investigated via GC-MS only in Regime 2, as the combustion process, particularly at low temperatures, allows for the preservation of only semi-volatile organic substances within the mineral matrix. The mass chromatograms of the ash samples are presented in Figures 11–12.

Analysing the mass chromatograms of the soot samples (Figs. 7–10), a group of markers indicating the thermal degradation of wood biomass was identified, primarily in Regime 1. The principal marker is levoglucosan (1,6-anhydro-beta-D-glucopyranose) – the dominant peak No. 18 in soot 1, accounting for 27.19 % of the area. Notably, it is not detected in Regime 2,

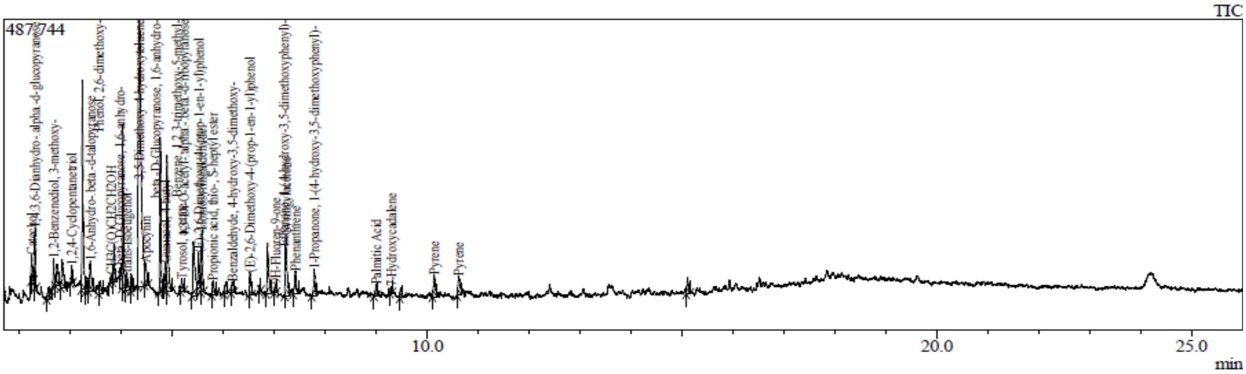


Fig. 7. TIC of Soot 1 in Regime 1.

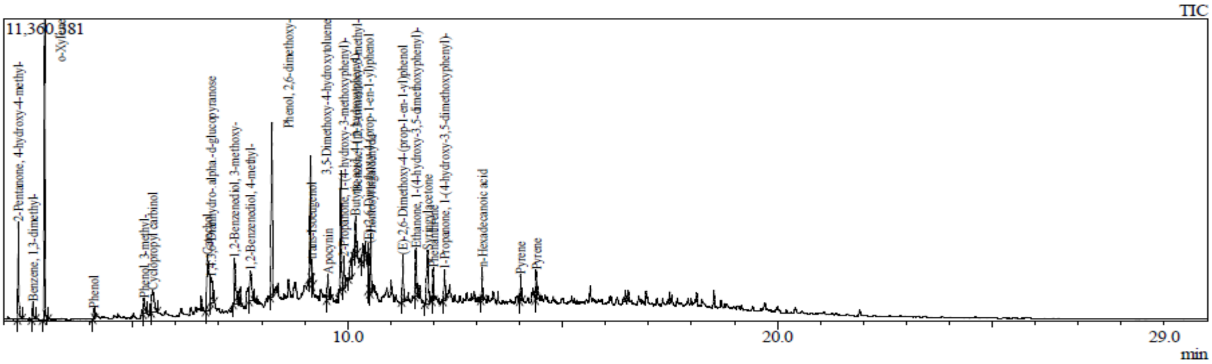


Fig. 8. TIC of Soot 1 in Regime 2.

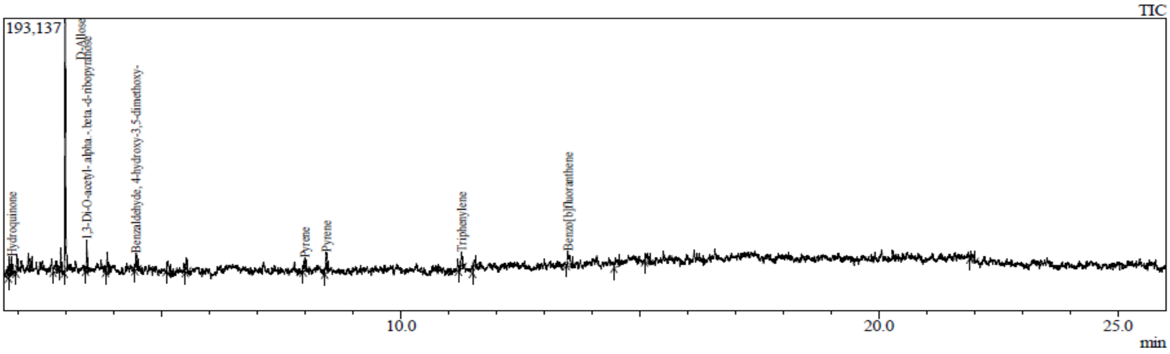


Fig. 9. TIC of Soot 2 in Regime 1.

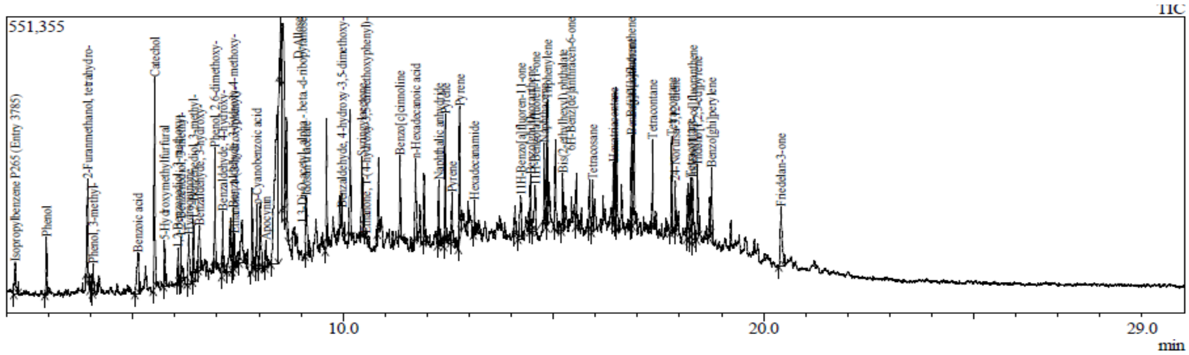


Fig. 10. TIC of Soot 2 in Regime 2.

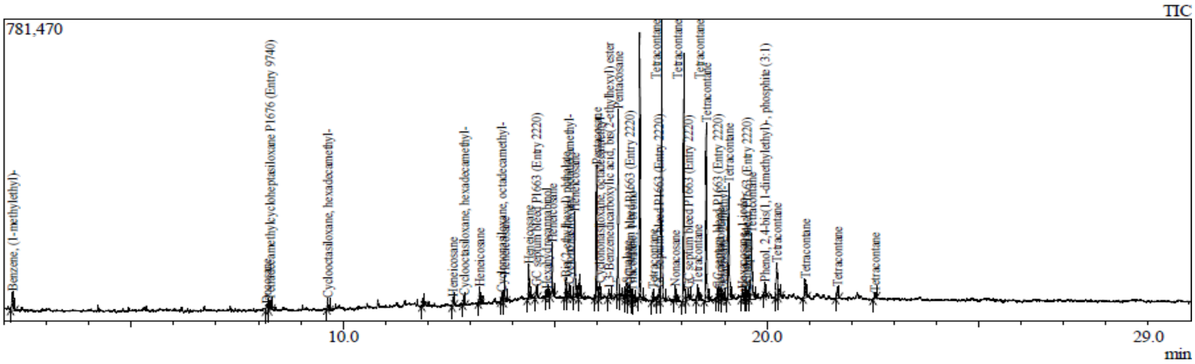


Fig. 11. TIC of Ash 1 in Regime 2.

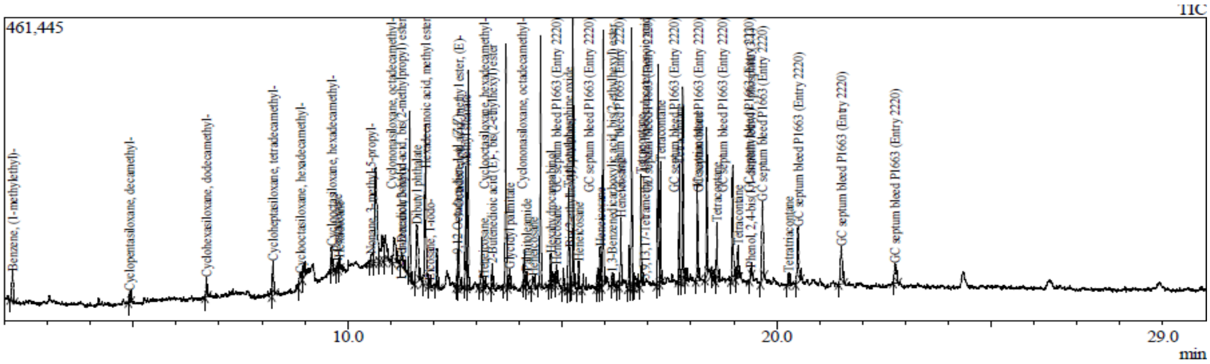


Fig. 12. TIC of Ash 2 in Regime 2.

suggesting that Regime 1 is characterised by the accumulation of oxygen-containing compounds resulting from the thermal decomposition of cellulose [14]. Furthermore, lignin degradation products – a group of methoxyphenols – were predominantly identified in Regime 1, specifically guaiacol (2-methoxyphenol) (peak No. 10, 3.42 %), creosol (phenol, 2-methoxy-4-methyl) (peak No. 14, 2.15 %), and syringol (2,6-dimethoxyphenol) (peak No. 22, 1.88 %) [17]. The preservation of methophilic groups in Soot 1 directly correlates with the high potassium content (K_{en} = 3.16), indicating a moderate combustion temperature at which the lignin structure breaks down into monomeric phenols but does not undergo full aromatisation. Conversely, in Regime 2, complete degradation of the carbohydrate fraction is observed. The primary chemical process shifts to aromatisation, leading to the emergence of PAHs. However, in Soot 1, synthesis largely halts at the stage of less condensed systems such as anthracene (peak No. 34, 1.12 %) and phenanthrene (peak No. 32, 4.56 %) [18], which is attributed to the baseline level of catalytic metal content [19]. The presence of light phenols and monosaccharides indicates the initial stages of biomass destruction, where the activation energy is insufficient for the formation of cyclic structures. Thus, Regime 2 for Soot 1 represents the activation threshold of the HACA mechanism [20], although the formation of heavy polycyclic systems remains moderate. This confirms that under conditions of metal deficiency (Zn, Fe), synthesis stops at anthracene structures, which belong to the medium condensation group.

In Soot 2, the concentration of levoglucosan in Regime 1 was significantly lower (approximately 2 %); instead, its isomer 1,4,3,6-dianhydro-D-glucopyranose was present (peak No. 8, 3.02 %). The low levoglucosan content in Soot 2 indicates a higher flame temperature, causing levoglucosan to undergo further thermal cleavage into smaller fragments, such as cyclopropyl carbinol (peak No. 6, 3.15 %) and 4-hydroxy-4-methyl-2-pentanone (peak No. 1, 4.07 %), signifying profound destruction of biomass hydrocarbon chains [21]. The concentration of methoxyphenols drops sharply to a total of less than 0.8 %, indicating extensive demethoxylation. This aligns with the XRF data regarding excess sulphur, as these temperatures facilitate the cleavage of sulphide and ether bridges [22].

Table 2.

Comparative composition of organic markers in soot and ash

Organic compound	Soot 1	Ash 1	Soot 2	Ash 2	Chemical role / origin
Levoglucosan	27.19	0.00	~2.00	0.00	Wood cellulose degradation
Methoxyphenols	7.45	0.00	0.80	0.00	Wood lignin degradation
D-Allose	0.00	0.00	48.37	0.00	Profound degradation of complex sugars
Medium PAHs C_{14+}	5.68	0.00	5.00	0.00	Anthracenes, phenanthrenes
Heavy PAHs C_{18+}	0.00	0.00	3.60	0.00	Anthropogenic benzofluoranthenes
Dibutyl phthalate	0.00	0.00	2.18	0.00	Plasticiser, PVC/waste marker
Heavy alkanes C_{30}–C_{40}	0.00	8.47	0.00	1.75	Aliphatic stabilisation by minerals
Cyclic siloxanes	0.00	0.55	0.00	0.80	Organosilicon: cosmetics/building materials

Transitioning to the analysis of Soot 2 in Regime 2, a significant leap in the complexity of the organic profile is observed compared to Soot 1. The aromatisation process intensifies: while Soot 1 was dominated by medium PAHs, Soot 2 exhibits highly condensed five-membered systems: benzo[k]fluoranthene (peak No. 54, 2.27 %), benzo[j]fluoranthene (peak No. 56, 1.33 %), pyrene (peak No. 48, 2.95 %), fluoranthene (peak No. 45, 3.12 %), and Chrysene (peak No. 52, 1.44 %). This represents a group of high-condensation PAHs [23]. A vital addition to the technogenic profile of Soot 2 in Regime 2 is the detection of dibutyl phthalate (peak No. 61, 2.18 %). Its presence in the volatile fraction serves as evidence of polymer material incineration, explaining the source of lead detected via XRF.

The higher content of transition metals in Soot 2, particularly Zn and Fe, compared to Soot 1, supports the hypothesis that Soot 2 acts as a more active catalytic environment for completing dehydrocyclisation reactions [19]. Unlike Soot 1, Soot 2 in Regime 1 shows an abnormally high content of D-allose (48.37 %), creating a stark contrast when transitioning to Regime 2, where sugars vanish entirely.

When applying Regime 2, patterns of selective substance distribution depending on the nature of the solid phase – carbonaceous or mineral – were traced. A comparative analysis of Soot 1 and its completely ashed product, Ash 1, revealed a thermal fractionation mechanism where the carbon matrix of Soot 1 acts as a selective sorbent for aromatic systems. Due to π-π interactions [23], polycyclic structures such as anthracenes and phenanthrenes are firmly retained on the soot surface, as described in previous studies. In Ash 1, PAH concentrations are virtually eliminated; however, an abnormally high content of ultra-heavy alkanes is recorded. Key markers include triacontane $C_{30}H_{62}$ (peak No. 38, 2.24 %) and tetracontane $C_{40}H_{82}$ (peak No. 40, 6.23 %). This proves that mineral centres (Fe, Ca) present in the ash have a higher affinity for long aliphatic chains, stabilising them at temperatures where aromatics desorb. Only in Ash 1 was hexadecamethyl-cyclooctasiloxane (peak No. 15, 0.55 %) identified, indicating specific sorption of organosilicon compounds onto the silicate components of the mineral phase [23].

For Soot 2 and Ash 2, the observed patterns repeat but with an intensification of toxic PAH synthesis in the soot. Unlike Soot 1, a significant accumulation of more complex systems is observed here – benzofluoranthenes totaling over 3.6 %. This is explained by the higher content of transition metal catalysts (Zn, Fe), which promote deep aromatisation specifically within the carbonaceous environment of the soot. In the mineral residue of Ash 2, heavy alkanes also predominate, with hexatriacontane $C_{36}H_{74}$ (peak No. 59, 1.75 %) being dominant. This confirms the general theory of mineral-organic encapsulation of higher alkanes, regardless of the initial soot type [15]. The siloxane content in Ash 2 is even higher than in Ash 1 (0.80 % for total cyclic siloxane peaks), correlating with XRF data showing high silicon content in this mineral matrix. This confirms the formation of a silicate matrix acting as a sorption container for heavy organics, protecting them from complete combustion via a silicate-driven stabilisation mechanism [24]. The comparative composition of organic markers in soot and ash is presented in Table 2.

Conclusions

The results of this study demonstrate the effectiveness and complementarity of the integrated XRF and GC-MS approach for identifying the nature of mixed fuels. The applied analytical strategy allowed not only for the verification of the elemental composition of the mineral residue but also for the differentiation of organic markers based on their volatility and molecular weight, which is crucial for the expert investigation of combustion products.

Specific patterns in the formation of the mineral phase depending on the fuel component composition were established. The detection of significant concentrations of zinc (0.952 %) and lead, alongside sulphur, in soot and ash samples indicates the degradation of inorganic fillers and pigments characteristic of synthetic polymeric materials. This confirms the transition of metal stabilisers from the condensed phase into the gas stream, with subsequent deposition on the soot surface.

Based on the identification of specific markers – levoglucosan and methoxyphenols – a mechanism for the degradation of cellulose and lignin has been proposed. The presence of dibutyl phthalate and heavy technogenic PAHs, such as benzofluoranthenes, in the combustion products indicates profound chemical transformations of synthetic hydrocarbon chains within the high-temperature zone.

The complex nature of the interaction between the organic and inorganic phases was revealed. It was established that the mineral components of the ash act as adsorption sites that stabilise heavy aliphatic hydrocarbons and cyclic siloxanes, preventing their complete thermal decomposition. The peak intensity ratios of PAHs with varying degrees of condensation indicate the catalytic role of finely dispersed metal oxides in the secondary aromatisation processes of pyrolysis products.

The proposed physicochemical approach enables the diagnostic assessment of the composition of incinerated raw materials. This has practical significance for environmental monitoring and forensic chemical analysis when identifying sources of illicit emissions and determining the causes of fires.

Notes

The authors declare no competing financial interest.

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Фізико-хімічне дослідження мінеральних та летких органічних продуктів термічного розкладу змішаного палива за допомогою рентгенофлуоресцентного аналізу (РФА) та газової хроматографії з мас-спектрометрією (ГХ-МС)

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У роботі представлені результати фізико-хімічного дослідження продуктів термодеструкції змішаного палива з використанням підходу, який поєднує методи рентгенофлуоресцентного аналізу (РФА) та хромато-мас-спектрометрії (ГХ-МС). Актуальність дослідження зумовлена потребою у створенні надійних критеріїв ідентифікації складу паливної сировини для потреб екологічного моніторингу та пожежно-технічної експертизи. Метою роботи було виявлення специфічних мінеральних та органічних маркерів у складі сажі та попелу, що дають змогу ідентифікувати природу спалюваних матеріалів.

Для аналізу було використане сучасне обладнання, що забезпечило високу точність визначення мікроелементного складу та ідентифікацію летких сполук. У ході дослідження встановлено, що мінеральна фаза продуктів горіння відображає наявність антропогенних домішок у паливі. Зокрема, у зразках, що містили компоненти побутового сміття та полімерів, виявлено значні концентрації цинку та свинцю на фоні сульфуру, що є наслідком деструкції неорганічних пігментів та стабілізаторів. ГХ-МС аналіз дозволив ідентифікувати маркери деструкції біомаси, такі як левоглюкозан і метоксифеноли, та зафіксувати появу дибутилфталату і важких поліядерних ароматичних вуглеводнів (ПАВ), що вказує на глибоку хімічну трансформацію синтетичних ланцюгів у високотемпературній зоні.

Дослідження міжфазної взаємодії підтвердило складний характер стабілізації органічних сполук мінеральною матрицею, а саме, що компоненти попелу виступають адсорбційними центрами для важких аліфатичних вуглеводнів та силоксанів, перешкоджаючи їх повному термічному розкладу. Співвідношення інтенсивностей піків ПАВ різного ступеня конденсації вказує на каталітичну роль оксидів металів у процесах вторинної ароматизації. Отримані результати підтверджують, що запропонований фізико-хімічний підхід є ефективним інструментом для діагностики складу спалюваної сировини, дозволяючи виявляти несанкціоноване використання шкідливих домішок та встановлювати причини антропогенного навантаження на довкілля.

Ключові слова: рентгенофлуоресцентний аналіз (РФА), хромато-мас-спектрометрія (ГХ-МС), термодеструкція змішаного палива, мінеральна фаза, попіл, важкі метали, сажа, органічні маркери, поліциклічні ароматичні вуглеводні (ПАВ), антропогенні маркери.