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Tests of volatile organic compounds in dust from hard coal preparation

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ABSTRACT

Coal dust can adsorb and retain volatile organic compounds (VOCs). This publication presented the identification and assessment of VOCs released from the dust from hard coal preparation plants. An original method combining the microchamber technique μ-CTE with thermal desorption and gas chromatography (TD-GC-MS) was employed. Identification of compounds was based on comparison of mass spectra with the NIST library and with the CRM EPA VOC Mixture 2 (target compounds) standard, which allowed for unambiguous identification of individual VOCs. Qualitative and quantitative analyses revealed a broad range of VOCs, including alkanes, carcinogenic benzene, and 2-ethyl-1-hexanol, a component of flotation reagents. Experiments were conducted using five variants differing in thermal extraction temperature and duration to assess the kinetics of VOC release. At 22 °C, the analytes were below the limit of quantification (LOQ), whereas at 65 °C and 90 °C, emission activation occurred, and extending extraction time to 60 minutes increased the amount of released compounds up to threefold. The results confirm the applicability of the μ-CTE method to evaluate the emission potential of coal dust and worker exposure risks, emphasizing the importance of selecting appropriate thermal extraction parameters for reliable and reproducible emission assessment.

Keywords: dust from hard coal preparation, volatile organic compounds (VOCs), VOCs emissions from dust, microchamber technique, thermal desorption, TD-GC-MS.

INTRODUCTION

The processes of hard coal preparation involve a series of technological operations, including crushing, classification, and beneficiation. These operations generate significant amounts of dust aerosols with a complex physicochemical structure [1–3]. Coal dust, characterized by a developed specific surface area and porous structure, constitutes an active matrix capable of adsorbing and retaining volatile organic compounds (VOCs), such as aromatic hydrocarbons (BTEX), phenols, or aldehydes [4–6]. Among them, there are substances classified as harmful, carcinogenic, and irritating. VOCs are capable of transferring from the coal matrix to the gas phase, and a determining factor of the kinetics of this phenomenon is thermal energy. Friction and impacts of the material in the processes of crushing and screening lead to local temperature increases, which promote the desorption of gases trapped in the organic structure of coal. The problem of VOCs release also occurs at the stage of storage of coal preparation waste [7]. Due to the low albedo (high darkness), these wastes have the ability to intensely absorb solar radiation. Studies show that under the conditions of high insolation, the surface layer temperatures of stockpiles can reach from 60 to 70 °C, and in the case of initiation of self-heating processes (low-temperature oxidation) exceed 90 °C [8–9]. Under such conditions, stockpiles become a secondary, large-area source of diffuse VOC emissions, affecting air quality. Another source of VOCs in the coal preparation process may be the process reagents added to flotation, serving as reagents imparting hydrophobicity to the surfaces of coal grains, frothing agents, modifiers improving flotation selectivity, and anti-caking agents [10].

Due to the documented toxic properties of VOCs, it is important to monitor their presence both in the occupational environment and in the external environment. The presence of VOCs in airborne dust fractions increases the risk of inhalation exposure, and long-term exposure may lead to respiratory system dysfunction, allergic reactions, organ damage, or an increased likelihood of developing cancers [11].

Studies of the dust accompanying the hard coal preparation process are widely described in the literature, covering both the characterization of the physicochemical properties of dusts and their harmfulness, as well as methods of mitigating this hazard [12–19]. However, the analyses conducted so far regarding the presence of VOCs have focused mainly on determining their concentrations in the air collected in mining face areas and in ventilation galleries of hard coal mines [20–21]. For this purpose, classical analytical techniques based on gas chromatography coupled with mass spectrometry (GC-MS), as well as advanced methods, such as photon-ionization time-of-flight mass spectrometry (PI-TOFMS), were used. These studies did not include the identification of the VOCs released from dust under conditions prevailing in coal preparation plants. This resulted from the lack of standardized analytical methods allowing the simulation of VOC release from bulk materials under controlled dynamic conditions. The available techniques allowed for the determination of the VOC content in dusts by solvent extraction, but they have significant limitations: evaporation leads to losses of volatile compounds, and at VOC boiling points close to the boiling points of the solvents used, this method becomes impossible to apply [22]. In this context, there is a visible need to conduct research on the methods for studying VOC release from the dust matrix, which will allow bridging the gap between the well-documented properties of coal preparation dust and the measurements of VOC concentrations in mine air.

This paper presented the results of research on the identification and assessment of the VOCs released from hard coal dust. The aim of the study was to determine the emission potential of the VOCs from particulate matter originating from hard coal preparation plants under various temperature–time conditions, as well as to gain insight into their desorption mechanisms. A novel research method combining microchamber techniques, in accordance with ISO 12219-3 and ISO 16000-6, and thermal desorption coupled with gas chromatography (TD-GC-MS), as applied in the automotive and construction industries, was employed [23–24].

MATERIALS AND METHODS

Sample collection and preparation

The study was conducted on the dust samples collected at a processing plant associated with a hard coal mine located in the Upper Silesian Coal Basin (GOP). The plant was selected based on the type of coal produced. At the chosen processing facility, coking coal of types 34 and 35 is produced, classified as a Critical Raw Material by the EU [25]. The coal processing technology employed at this plant is typical for coking coal production. The process includes crushing and classification of the raw coal, followed by enrichment using gravity methods in pulsating water jigs and, for the finest particles, froth flotation. These enrichment operations effectively separate tailings from the organic fraction, enabling the production of a concentrate with suitable coking properties. The enriched products are subsequently dewatered and homogenized to ensure a stable quality of the charge directed to the coke oven batteries.

Analysis of the coal preparation process and on-site inspection identified two areas with the highest dust concentrations, from which dust samples were collected for testing. These were located in the building of the Raw Coal Preparation Station for enrichment, in the vicinity of Bradford-type selective crushers and WK-type vibrating screens used for preliminary coal classification. At each location, three elementary dust samples were collected. The dust samples were placed in 25 mL glass containers with PTFE seals (zero headspace) and transported to the laboratory at 4 °C to minimize the loss of volatile fractions. In the laboratory, the elementary samples were combined to obtain two composite samples. The composite samples were labeled as follows: SD1 – dust sample from the Bradford crushers area, and SD2 – dust sample from the WK-type vibrating screens area. The SD1 sample contained, on average, 69 wt.% PM10, 30 wt.% PM2.5, and 29 wt.% PM1, whereas the SD2 sample contained 77 wt.% PM10, 34 wt.% PM2.5, and 32 wt.% PM1.

Chemicals and standards

The following materials and analytical standards were used in the study:

- Sorption tubes: Steel tubes packed with the Tenax TA sorbent (Markes International Ltd.) were used. Prior to each use, the tubes were thermally conditioned in a Tube Conditioner TC-20 for 30 minutes at 330 °C under a nitrogen flow of 5.0 purity (50 mL/min), ensuring a clean analytical background, which was confirmed by analysis of the tubes after conditioning.
- Analytical standards (CRM): Certified Reference Material (CRM) EPA VOC Mixture 2 (2000 µg/mL in methanol, LGC Group / DR EHRENSTORFER; Lot Number 2-H494166ME) was used for calibration and validation. A series of dilutions in HPLC-grade methanol (Merck) was prepared from the stock solution, yielding concentrations ranging from 10 to 1000 ng/µL.
- Standard application: Standards were applied in a volume of 1 µL onto Tenax TA tubes in the gas phase (nitrogen stream) using a CSLR (Calibration Solution Loading Ring, Markes International Ltd.) calibrator, simulating realistic sorption conditions. A reagent blank was prepared by applying 1 µL of methanol to a tube.
- Process reagents: The chemicals used in the flotation process were also analyzed, including a polymeric flocculant (polyacrylamide-based) and a flotation agent (a mixture of alcohols and esters). This analysis allowed the identification of chemical markers used to verify the contribution of these reagents to the total VOC emissions from the dust (e.g., 2-ethyl-1-hexanol).

Thermal extraction (µ-CTE procedure)

Volatile organic compounds (VOCs) from the dust samples were released using thermal extraction with a µ-CTE 250 microchamber (Markes International Ltd., UK). To evaluate the effect of extraction parameters on the amount of VOCs released, five experimental variants (A-E), were applied, differing in extraction temperature and duration. The extraction temperatures were chosen to reflect environmental conditions occurring during the coal preparation process, such as crushing and screening of the raw material, and to simulate elevated thermal loads characteristic of waste storage sites, including the *worst-case scenario* conditions. The chosen temperatures were 22 °C, 65 °C, and 90 °C. These temperature values were based on the published protocols for VOC emission studies from complex matrices (e.g., construction materials and polymers used in the automotive industry) [23,26]. The extraction time was varied according to each variant to characterize the kinetics of VOC release. The mass of dust subjected to extraction was 100 mg. Other extraction parameters, including carrier gas type (Nitrogen 5.0), flow rate (70 mL/min), and pressure (89.6 kPa), were kept constant across all experimental variants to eliminate the influence of instrumental variables on the results. Detailed extraction conditions for each variant are presented in Table 1.

In each experimental variant, four parallel samples taken from the composite samples SD1 and SD2 were analyzed. Before starting the extraction, the chambers containing the dust samples were conditioned for 20 minutes at the set temperature under a constant carrier gas flow to achieve thermal equilibrium. VOCs were then transferred by the gas stream to sorption tubes, where they were captured.

TD-GC-MS analysis

The collected compounds were analyzed using a TD100-xr thermal desorber (Markes) coupled to a GC-MS system (e.g., Agilent 7890B/5977B), following the analytical protocol presented in Table 2.

To verify the performance of the analytical system, the EPA VOC Mixture 2 standard was analyzed. Figure 1 shows the chromatogram (TIC – total ion chromatogram) obtained from the analysis, demonstrating proper separation of the analytes under the applied chromatographic conditions. Detailed parameters for analyte

Table 1. µ-CTE 250 (markes) extraction conditions

Extraction conditions	Experimental variants				
	A	B	C	D	E
Extraction time [min]	60	15	60	30	60
Extraction temperature [°C]	22	65	65	90	90

Table 2. TD-GC-MS analysis (based on [27])

Analysis stage	Analysis conditions	
	Device type	Parameters
I	TD100-xr	• Cold trap: General-purpose carbon • Tube desorption: 250 °C / 10 min • Trap: Low / High temperature 25 °C / 300 °C, Desorbtion time: 5 min • Purge time: 1 min • Flow: 50 ml/min (Purge, Trap, Split)
II	GC System	• Inlet: Splitless • Column: HP-5ms (30 m × 0.25 mm × 0.25 μm) • Helium: 1.5 ml/min • Oven: 40 °C (5 min) then 10 °C/min to 200 °C
III	MSD	• Ionization type: EI • Acquisition type: SCAN • Source temperature: 230 °C • Quad temperature: 150 °C

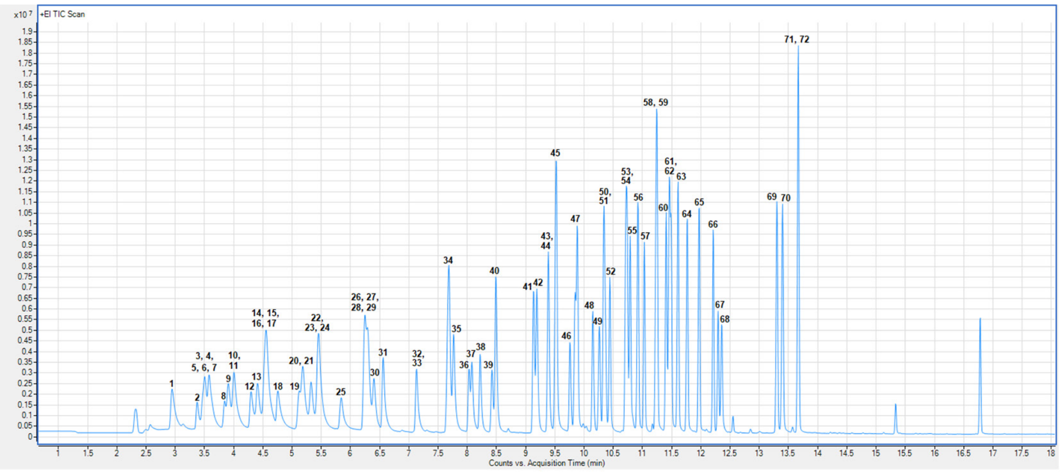

Figure 1. Total ion chromatogram of target compounds in EPA VOC mixture 2 CRM (1000 ng per tube)

identification, including retention times and quantification ions (quant), are summarized in Table 3.

Method validation and quality control

To ensure the repeatability and reliability of the results, the developed TD-GC-MS analytical protocol was validated in accordance with the ICH (International Council for Harmonisation) guidelines. The validation included determination of the following method parameters: linearity, sensitivity (LOD, LOQ), and precision. Calibration curves were prepared at five concentration levels (10, 50, 100, 500, 1000 ng analyte per tube). High linearity was observed for all tested compounds, as confirmed by correlation coefficients (R^2) above 0.995. The limits of detection (LOD) and quantification (LOQ) were determined based on the signal-to-noise ratio (S/N), adopting values of 3:1 and 10:1, respectively. These values confirm the high sensitivity of the method, allowing the detection of trace VOC emissions at lower temperatures (22 °C). Precision was expressed as the relative standard deviation (RSD%) from five independent replicates (n = 5). For all tested compounds, RSD did not exceed 10%. Validation parameters of the TD-GC-MS method for selected VOCs are presented in Table 4.

The obtained validation parameter values confirm the correctness of the developed method.

Data analysis

Qualitative and quantitative analysis of VOCs was performed with reference to the CRM EPA VOC Mixture 2 (target compounds) based on retention times and mass spectra. Calibration curves were constructed over a concentration range of 10–1000 ng. For other compounds, analysis was carried out using the Unknowns Analysis module in the Agilent software. Background signals from conditioned tubes were taken into account in all analyses.

Table 3. Target compounds in EPA VOC Mixture 2 CRM

Peak ID	Compound name	CAS number	Quantifier ion (m/z)	RT (min)
1.	diethyl ether	60-29-7	59.1	3.37
2.	carbon disulfide	75-15-0	76.0	3.50
3.	1,1-dichloroethene	75-35-4	61.0	3.50
4.	iodomethane	74-88-4	142.0	3.50
5.	acrylonitrile	107-13-1	53.0	3.50
6.	allyl chloride	107-05-1	76.0	3.51
7.	methylene chloride	75-09-2	84.0	3.58
8.	trans-1,2-dichloroethene	156-60-5	61.0	3.84
9.	methyl tert-butyl ether	1634-04-4	73.1	3.91
10.	propionitrile	107-12-0	28.0	4.00
11.	1,1-dichloroethane	75-34-3	63.0	4.01
12.	acrylonitrile	126-98-7	41.0	4.30
13.	cis-1,2-dichloroethene	156-59-2	61.0	4.40
14.	bromochloromethane	74-97-5	49.0	4.55
15.	chloroform	67-66-3	83.0	4.55
16.	methyl acrylate	96-33-3	55.0	4.56
17.	2,2-dichloropropane	594-20-7	77.0	4.56
18.	tetrahydrofuran	109-99-9	42.0	4.75
19.	1,1,1-trichloroethane	71-55-6	97.0	5.12
20.	1-chlorobutane	109-69-3	56.0	5.18
21.	1,2-dichloroethane	107-06-2	62.0	5.18
22.	1,1-dichloropropene	563-58-6	75.0	5.44
23.	carbon tetrachloride	56-23-5	117.0	5.44
24.	benzene	71-43-2	78.0	5.44
25.	chloroacetonitrile	107-14-2	75.0	5.84
26.	1,2-dichloropropane	78-87-5	63.0	6.23
27.	trichloroethene	79-01-6	95.0	6.24
28.	dibromomethane	74-95-3	93.0	6.26
29.	2-nitropropane	79-46-9	43.0	6.30
30.	bromodichloromethane	75-27-4	83.0	6.40
31.	methyl methacrylate	80-62-6	69.0	6.56
32.	cis-1,3-dichloropropene	10061-01-5	75.0	7.13
33.	trans-1,3-dichloropropene	10061-02-6	75.0	7.13
34.	toluene	108-88-3	91.0	7.68
35.	1,1,2-trichloroethane	79-00-5	97.0	7.76
36.	1,3-dichloropropane	142-28-9	76.0	8.03
37.	ethyl methacrylate	97-63-2	69.0	8.08
38.	dibromochloromethane	124-48-1	129.0	8.21
39.	1,2-dibromomethane	106-93-4	107.0	8.42
40.	tetrachloroethene	127-18-4	166.0	8.48
41.	chlorobenzene	108-90-7	112.0	9.12
42.	1,1,1,2-tetrachloroethane	630-20-6	131.0	9.19
43.	ethylbenzene	100-41-4	91.0	9.30
44.	bromoform	75-25-2	173.0	9.36
45.	m,p-xylene (sum)	108-38-3 / 106-42-3	91.0	9.51
46.	styrene	100-42-5	104.0	9.84
47.	o-xylene	95-47-6	91.1	9.88

Table 3. Cont.

48.	1,1,2,2-tetrachloroethane	79-34-5	83.0	10.15
49.	1,2,3-trichloropropane	96-18-4	110.0	10.26
50.	isopropylbenzene	98-82-8	105.0	10.34
51.	trans-1,4-dichloro-2-butene	110-57-6	75.0	10.36
52.	bromobenzene	108-86-1	156.0	10.44
53.	2-chlorotoluene	95-49-8	91.0	10.71
54.	n-propylbenzene	103-65-1	91.0	10.72
55.	4-chlorotoluene	106-43-4	91.0	10.78
56.	1,3,5-trimethylbenzene	108-67-8	105.0	10.92
57.	pentachloroethane	76-01-7	167.0	11.03
58.	tert-butylbenzene	98-06-6	119.0	11.24
59.	1,2,4-trimethylbenzene	95-63-6	105.0	11.24
60.	1,3-dichlorobenzene	541-73-1	146.0	11.40
61.	sec-butylbenzene	135-98-8	105.0	11.45
62.	1,4-dichlorobenzene	106-46-7	146.0	11.49
63.	4-isopropyltoluene	99-87-6	119.0	11.61
64.	1,2-dichlorobenzene	95-50-1	146.0	11.77
65.	n-butylbenzene	104-51-8	91.0	11.97
66.	hexachloroethane	67-72-1	200.0	12.20
67.	1,2-dibromo-3-chloropropane	96-12-8	157.0	12.29
68.	nitrobenzene	98-95-3	77.0	12.35
69.	1,2,4-trichlorobenzene	120-82-1	180.0	13.30
70.	naphthalene	91-20-3	128.0	13.40
71.	hexachlorobutadiene	87-68-3	180.0	13.66
72.	1,2,3-trichlorobenzene	87-61-6	182.0	13.66

Table 4. Validation parameters of the TD-GC-MS method for selected VOCs

Compoud name	Range [ng]	Regression equation	R^2	LOD [ng]	LOQ [ng]	RSD%
benzene	10–1000	$y=8233 \cdot x+80814$	0.9997	4.15	13.8	7.2
ethylbenzene	10–1000	$y=9631 \cdot x+42492$	0.99996	8.0	26.8	9.0
m,p-xylene	10–1000	$y=12721 \cdot x+256563$	0.9993	5.1	17.2	6.0
o-xylene	10-1000	$y=8210 \cdot x+22128$	0.9997	3.9	13.1	8.3
styrene	10–1000	$y=4131 \cdot x+38516$	0.9990	3.2	8.4	9.3
toluene	10-1000	$y=12553 \cdot x+31705$	0.9996	11.4	38.1	8.8
1,2,4-trimethylbenzene	10-1000	$y=8370 \cdot x+49360$	0.99994	15.1	50.6	8.6

Compound identification was based on the analysis of individual peak spectra and the match factor (MF), which ranges from 0 to 100 and indicates the degree of agreement between the mass spectrum of the analyzed compound and the reference spectrum in the NIST Tandem Mass Spectral Library Version 2.3 (2017). A match factor of MF > 80 was used as the identification criterion.

RESULTS

Qualitative analysis

The results of the qualitative analysis, presented as chromatographic profiles of volatile organic compounds released from dust samples SD1 and SD2, are shown in Figure 2 for temperatures of 22 °C, 65 °C, and 90 °C.

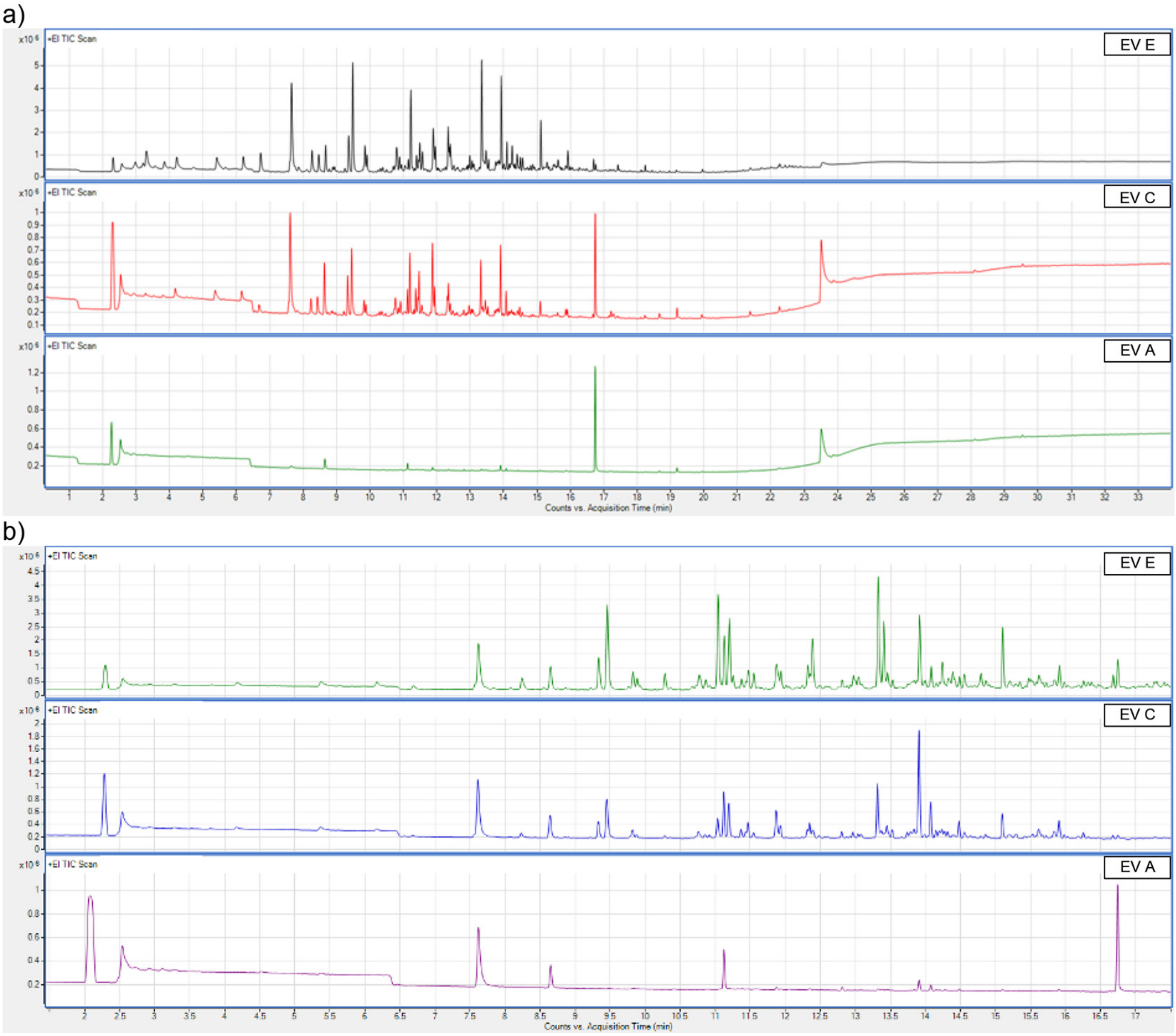

Figure 2. Comparison of TIC chromatograms after extraction using experimental variants (EVs) A, C, and E for dust samples: (a) SD1, (b) SD2

Analysis of the chromatograms (TIC) revealed a wide spectrum of volatile organic compounds (VOCs) released from dust samples SD1 and SD2. VOC signal intensity increased with thermal extraction temperature. At 65 °C (experimental variant C) and 90 °C (experimental variant E), VOC release was triggered, whereas at lower temperatures, such as 22 °C (experimental variant A), many compounds remained trapped within the porous coal structure.

The list of VOCs identified for experimental variants C and E, which featured the longest extraction time (60 min), using the Unknowns Analysis module, is presented in Table 5. For each compound, the chemical name, molecular formula, CAS number, compound type (aromatic hydrocarbon, alkane, amide, ester/isocyanate, acid, fatty acid), and classification were provided, indicating VOC subgroups distinguished by volatility, boiling point, and odor intensity: VVOC (very volatile organic compounds), SVOC (semi-volatile organic compounds), and VOV (very odorous volatiles).

Analysis of the results summarized in the table showed that the dominant groups were aliphatic hydrocarbons (alkanes) and benzene, accounting for over 57% of the identified compounds. The largest number of compounds was released at 90 °C from dust sample SD2 (experimental variant E). The particularly hazardous aromatic hydrocarbon benzene, which is carcinogenic, was released at 65 °C (experimental variant C). The results also showed the release of 2-ethyl-1-hexanol, classified as a VOV, from both SD1 (experimental variant E) and SD2 (experimental variants C and E). This compound is not a natural constituent of coal macerals, but may be present as a component of the flotation reagent.

Table 5. Results of unknowns analysis

Sample	Compoud name	Molecular formula	CAS number	Compound type	Compound class
SD1	Experimental variant C (temp. 65 °C)				
	benzene	C_6H_6	71-43-2	aromatic hydrocarbon	VOC
	pentane	C_5H_{12}	109-66-0	alkane	VOC
	n-hexane	C_6H_{14}	110-54-3	alkane	VOC
	Experimental variant E (temp. 90 °C)				
	butane	C_4H_{10}	106-97-8	alkane	VVOC
	2-methylbutane	C_5H_{12}	78-78-4	alkane	VVOC
	2-methylpentane	C_6H_{14}	107-83-5	alkane	VOC
	tetracosane	$C_{24}H_{50}$	646-31-1	alkane	SVOC
	2-ethyl-1-hexanol	$C_8H_{18}O$	104-76-7	alcohol	VOV
SD2	Experimental variant C (temp. 65 °C)				
	n-hexane	C_6H_{14}	110-54-3	alkane	VOC
	heptane	C_7H_{16}	142-82-5	alkane	VOC
	2-ethyl-1-hexanol	$C_8H_{18}O$	104-76-7	alcohol	VOV
	Experimental variant E (temp. 90 °C)				
	pentane	C_5H_{12}	109-66-0	alkane	VVOC/VOC
	n-hexane	C_6H_{14}	110-54-3	alkane	VOC
	tetracosane	$C_{24}H_{50}$	646-31-1	alkane	SVOC
	2-ethyl-1-hexanol	$C_8H_{18}O$	104-76-7	alcohol	VOV
	hydrazinecarboxamide (semicarbazide)	CH_5N_3O	57-56-7	amide	VOC
	butyl isocyanatoacetate	$C_7H_{11}NO_3$	17046-22-9	ester/ isocyanate	VOC
	2-octyl palmitate	$C_{24}H_{48}O_2$	55194-81-5	ester	SVOC
	acetic acid	C_2H_4O	64-19-7	acid	VOC
	n-hexadecanoic acid (palmitic acid)	$C_{16}H_{32}O_2$	57-10-3	fatty acid	SVOC

The obtained match factor (MF) values, confirming the agreement between the mass spectra of the individual VOCs and the reference spectra in the NIST Tandem Mass Spectral Library, are presented in Figure 3.

Analysis of the results presented in the figure showed that the highest match factor (MF) with reference spectra from the NIST Library was obtained for 2-ethyl-1-hexanol and n-hexane (MF = 97). The obtained MF values for the spectra of the analyzed compounds met the adopted matching criterion (>80).

Quantitative analysis

The results of the quantitative analysis obtained for the five experimental variants, differing in thermal extraction temperature and time, and performed with reference to the CRM EPA VOC Mixture 2 (target compounds), are presented in Table 6. Analysis of the results presented in Table 4 showed that dust samples SD1 and SD2 released benzene and its derivatives: toluene, ethylbenzene, and xylenes (o-, m-, p-), classified as BTEX, as well as tetrachloroethene, naphthalene, and 1,2,4-trimethylbenzene. Measurable amounts of benzene, m,p-xylene, and tetrachloroethene were detected at 65 °C. The 1,2,4-trimethylbenzene and naphthalene compounds were released from both samples at 90 °C. At 22 °C (experimental variant A), the concentrations of all analytes from the target compounds group in SD1 and SD2 were below the method's limit of quantification (LOQ), suggesting that under static conditions, the dust exhibits a high sorption capacity. Additional analyses of the chemical reagents used in the flotation process did not reveal any compounds overlapping with the analyzed VOCs. The amounts of BTEX released from the dust samples, as well as their totals for the experimental variants (EV: B-E), are presented in Figure 4.

Figure 3. Match factor of identified VOCs

Table 6. Results of quantitative analysis

Sample	EV	Amount of VOCs released [µg/g dust]							
		benzene	toluene	ethylbenzene	m,p-xylene	o-xylene	tetrachloro-ethene	naphthalene	1,2,4-trimethyl-benzene
SD1	A	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	ND	ND	ND	ND	0.20 ±0.01	ND	ND
	C	0.13 ±0.01	ND	ND	0.19 ±0.03	ND	0.27 ±0.02	ND	ND
	D	0.43 ±0.03	0.85 ±0.07	0.42 ±0.05	1.48 ±0.02	0.54 ±0.03	0.60 ±0.07	0.19 ±0.01	0.35 ±0.02
	E	0.71 ±0.11	3.74 ±0.2	0.90 ±0.04	2.90 ±0.14	1.06 ±0.03	0.96 ±0.04	0.62 ±0.10	1.01 ±0.11
SD2	A	ND	ND	ND	ND	ND	ND	ND	ND
	B	ND	ND	ND	ND	ND	ND	ND	ND
	C	ND	ND	ND	0.17 ±0.01	ND	ND	ND	ND
	D	0.18 ±0.02	ND	0.41 ±0.04	1.14 ±0.02	0.34 0.01	ND	0.13 ±0.01	0.23 ±0.03
	E	0.26 ±0.08	ND	0.74 ±0.06	1.86 ±0.15	0.62 ±0.05	ND	0.37 ±0.01	0.48 ±0.04

Note: EV – experimental variant; ND (not detected) – < LOQ; All analyses were performed for four parallel samples (n = 4), and the results are presented as mean ± standard deviation (SD).

Analysis of the data presented in Figure 4 showed that the highest mass of BTEX compounds was released from sample SD1 using experimental variant E (> 9.3 µg/g of dust). The qualitative analysis results confirmed the release of benzene at 65 °C with an extraction time of 60 min. Under these conditions, m- and p-xylenes were released from both dust samples. Toluene was not detected in sample SD1. At 90 °C, an increase in extraction time resulted in higher amounts of released BTEX.

Release kinetics of VOCs

Comparison of the amounts of VOCs released at 90 °C, as determined by quantitative analysis (Table 6), with respect to the thermal extraction times applied in the experimental variants, allowed characterization of the kinetics of their release from the dust samples. The analysis showed that the short extraction time (15 min) at 65 °C resulted in analyte concentrations from the target compounds group in SD1 and SD2 being

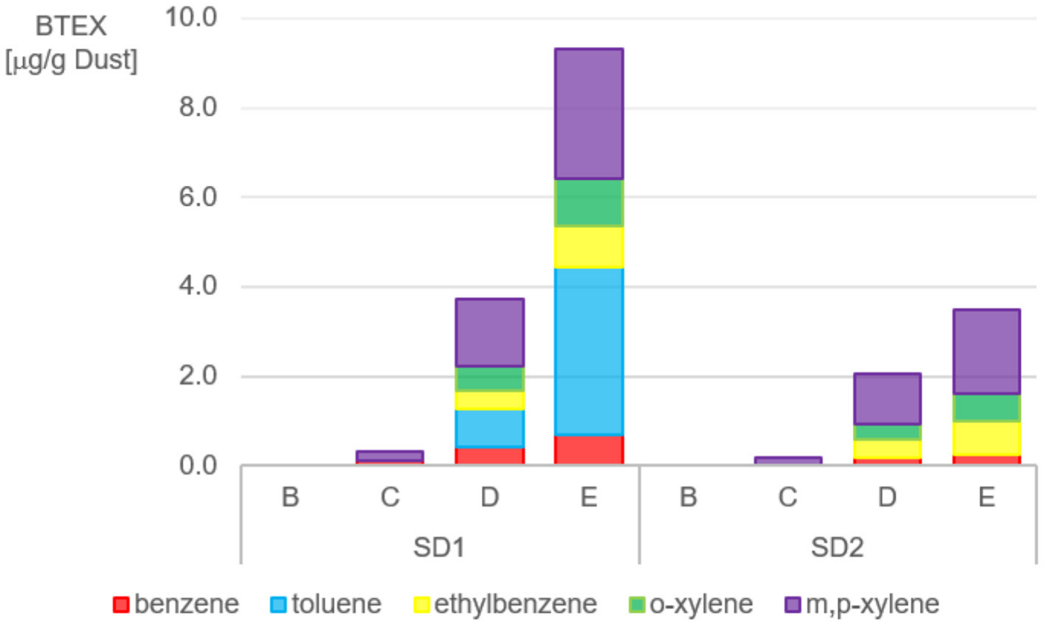

Figure 4. Amounts of BTEX released from dust samples SD1 and SD2

at or near the limit of detection, with the exception of tetrachloroethylene, which was identified. Extending the extraction time to 60 min at this temperature revealed measurable concentrations of these compounds, indicating slow physical diffusion from the micropores of the coal matrix. A continuous increase in the amount of released VOCs was observed when the extraction time was extended from 30 to 60 min at 90 °C, with the highest increases recorded for toluene, naphthalene, and 1,2,4-trimethylbenzene. The increases were as follows: toluene, 340%; naphthalene, 226% (sample SD1) and 185% (sample SD2); 1,2,4-trimethylbenzene, 189% (sample SD1) and 109% (sample SD2). For tetrachloroethylene, extending the extraction time from 15 to 30 min at 65 °C and from 30 to 60 min at 90 °C resulted in an increase in its released amount by over 60%. The effect of extraction time on VOC release is shown in Figure 5.

The graphs presented in Figure 5 indicate that VOC release at 90 °C does not reach a plateau. This suggests a change in the nature of the emission – from diffusion-controlled kinetics (depletion of the reservoir) to a continuous process.

DISCUSSION

The microchamber technique µ-CTE, adapted for a novel research method, enables the simulation of VOC release from dust samples into the air under conditions reflecting the environmental parameters present in a hard coal preparation plant, as well as at post-mining waste storage sites. The results obtained under experimental conditions allowed determination of the types and potential amounts of VOCs that may be emitted from the studied dusts. This represents a significant advantage over solvent extraction techniques, which only allow quantification of the total content of all compounds present in the dust, without providing information on their potential emission into the air. These findings confirm the validity of using the µ-CTE technique to assess the real risk of exposure to the VOCs released from dust. For the application of this method, the appropriate selection of thermal extraction parameters is essential, as they have a significant impact on the amounts of compounds released. As it is shown by the experimental results, the procedures with short extraction times (15–30 minutes) may underestimate these amounts by up to 50%, compared to the results obtained with longer extraction times (60 minutes).

The effectiveness of the developed and validated TD-GC-MS analytical algorithm, applied for the identification of individual VOCs released during thermal extraction, is confirmed by the high agreement of mass spectra with the NIST library. For key volatile compounds, such as n-hexane, butane, pentane, and heptane, the obtained Match Factor values exceeded 90, allowing their unambiguous identification (so-called confident identification). The identified compounds served as the basis for

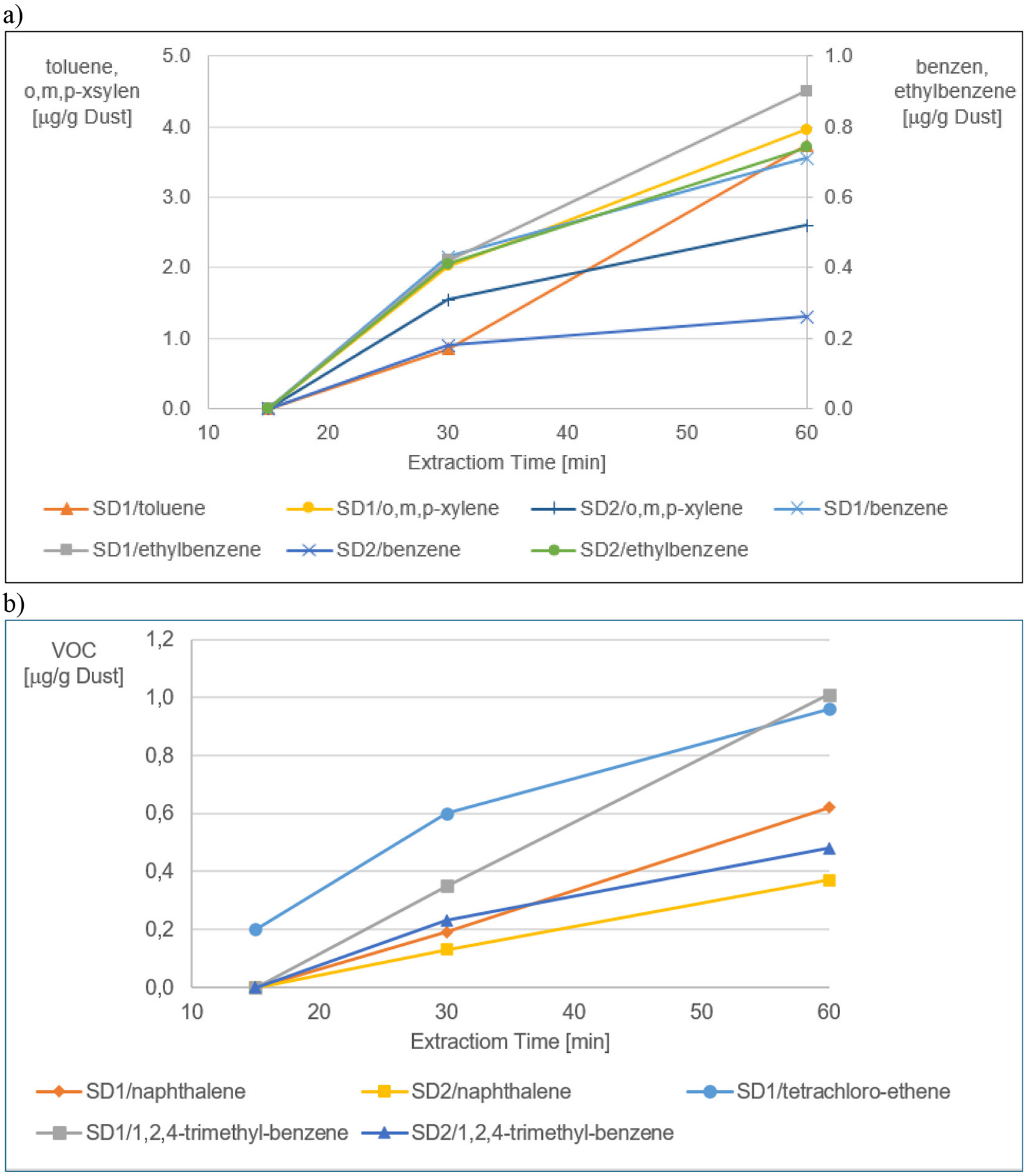

Figure 5. Effect of extraction time on the amount of VOCs released: (a) BTEX, (b) compounds other than BTEX

selecting analytes for quantitative analysis using the certified EPA VOC Mixture 2 standard.

Among the volatile compounds released from the studied dusts, all subgroups – VVOCs, VOCs, and SVOCs – relevant for air quality assessment were detected. The presence of a VOV compound with a strong odor, 2-ethyl-1-hexanol, a component of the flotation reagent, was also confirmed [28-29]. Its detection indicates that the coal dust in preparation plants acts as a carrier for synthetic chemical additives, which significantly modifies the toxicological profile of emissions compared to raw coal.

The identification of benzene release from dust samples SD1 and SD2 is particularly important for human health protection, including workers in the coal preparation plant, as this compound is carcinogenic and classified as Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC). Its presence, along with other harmful substances confirmed by the study, such as xylenes and 1,2,4-trimethylbenzene – classified as neurotoxic compounds – highlights the need for their monitoring as markers of air pollution in preparation plants.

The dynamics of VOC release from coal dust depend on the applied thermal stress. At 65 °C, physical thermal desorption predominates. The presence of volatile alkanes (pentane, n-hexane) and benzene under these conditions results from the release of gases secondarily trapped in the expanded, microporous structure of coal (so-called ink-bottle pores). A change in the release mechanism occurs at 90°C. The absence of a plateau in the kinetic curve during 60 minutes of extraction may indicate the initiation of low-temperature coal oxidation processes (LTO – low-temperature oxidation) [30]. Confirmation of this phenomenon requires further investigation. It would be important to determine the threshold temperatures above which successive release mechanisms become activated – from physical desorption, through diffusion-assisted desorption, to the chemical reactions associated with oxidation. For this purpose, it is advisable to extend the experimental range with additional temperature variants covering the 22–90 °C interval, using smaller temperature increments. This will allow for precise identification of the transition points between individual mechanisms and for the development of a more detailed kinetic model of VOC release from the dust matrix.

CONCLUSIONS

The study demonstrated that the dust from hard coal preparation plants is an active source of volatile organic compound (VOC) emissions, with both the intensity and composition depending on the temperature and duration of exposure. Qualitative analysis confirmed the presence of a wide spectrum of VOCs, dominated by alkanes and the carcinogenic benzene. The presence of hydrophobic 2-ethyl-1-hexanol, a component of flotation reagents, indicates the potential for modification of the surface properties of the dust, which may enhance the adsorption of other pollutants.

Quantitative analysis confirmed the release of compounds of significant toxicological concern, including benzene, toluene, ethylbenzene, xylenes, 1,2,4-trimethylbenzene, tetrachloroethene, and naphthalene. At 22 °C, the concentrations of all analytes remained below the LOQ, indicating the strong sorptive properties of the dust under static conditions. Increasing the temperature to 65 °C and 90 °C led to a rapid activation of emissions, while extending the extraction time to 60 minutes increased the amounts of released compounds by up to threefold.

Kinetic analysis of VOC release showed that at 65 °C, physical thermal desorption of gases trapped in micropores predominates, whereas at 90 °C, the process becomes continuous, indicating the onset of low-temperature coal oxidation (LTO). This means that under elevated temperature conditions, coal ceases to act as a passive sorbent and instead functions as an active reactor generating new oxidation products.

The results of the study confirmed that the developed original method, employing the microchamber technique, provides an effective tool for assessing the real emission potential of dusts. High agreement of the mass spectra with the NIST library confirmed the reliability of compound identification. At the same time, it was demonstrated that short thermal extraction times (15–30 minutes) lead to a significant underestimation of emissions, which is critical for evaluating worker exposure and air quality in preparation plants.

Despite the demonstrated advantages and utilitarian applicability of the method, further refinement is recommended, particularly with regard to the thermal extraction parameters, aiming to determine the threshold temperatures for the release of individual VOC groups under environmental conditions.

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