Green Foundry LIFE project (LIFE17 ENV/FI/000173)

AGH –UNIVERSITY OF SCIENCE AND TECHNOLOGY ACTIONS
Action B1: Emissions of different binder systems during small – scale test casts.
Method 2. Tests in foundry plants – small scale chamber

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1. Material and scope of research

Research on the composition of gases (BTEX and PAHs groups) formed during pouring and cooling of molds and knocking out of castings were conducted in the HARDKOP foundry in Trzebinia. Six types of molding sands were selected for testing. The schedule showing the order of research (sampling) in the HARDKOP foundry along with the types of masses used are described in Table 1. Ratio mould sand : metal was 2.8 – 3.0. Temperature of liquid cast iron was 1380 – 1420^{o}C.

Table 1. Schedule of meltings together with the types of moulding sands

Test No.	Type of mould sand	Technology of moulding sands	Description of the sample used in the report
1	MF	Mouuld sand with furan resin	PAH Test 1 BTEX Test 1
2	MA	Mould sand with phenol – formaldehyde resin	PAH Test 2 BTEX Test 2
3	MB	Greensand	PAH Test 3 BTEX Test 3
6	M I	Mould sand INOTEC binder	PAH Test 6 BTEX Test 6
8	MG	Mould sand with GEOPOL binder	PAH Test 8 BTEX Test 8
9	MC	Mould sand with CORDIS binder	PAH Test 9 BTEX Test 9

Prepared molds were placed on a vibrating table, the construction of which, after the pouring and cooling of the mold, allow knocking out the casting, without having to dismantle the stand. The whole system was placed in a metal box with a flap opened in the upper part, through which liquid metal was poured into the mold. The box was equipped with a connector, through which gases generated in the process were sucked. The scheme of the measuring stand is shown in Figure 1.

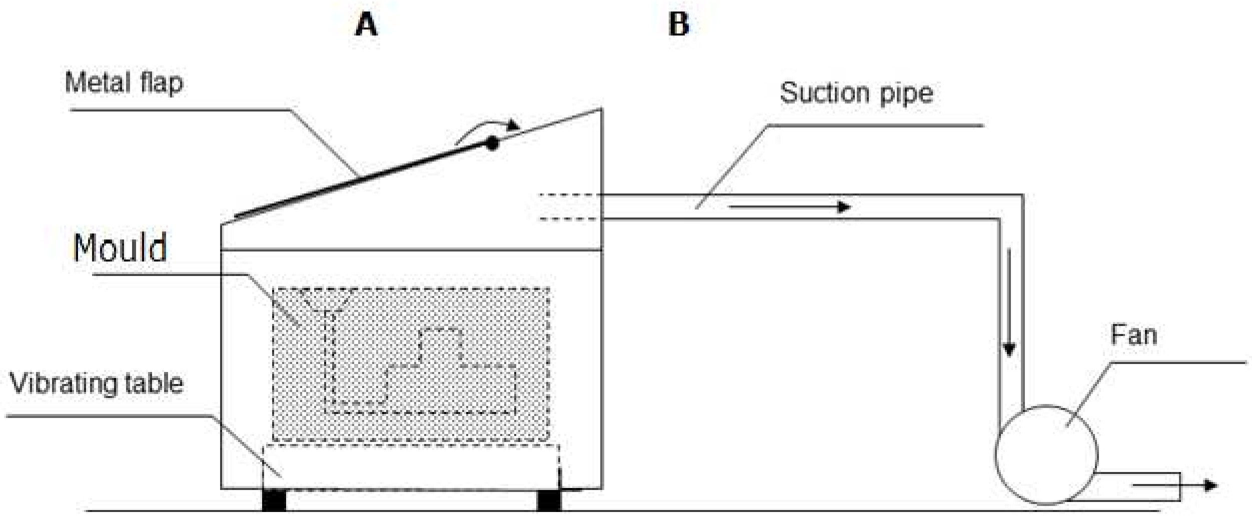

Fig. 1. The scheme of the stand for pouring, cooling and shaking-out:
a) pouring stand, b) suction system

The process of releasing gases from a mold flooded with liquid metal occurs intensively in the first few minutes of flooding and with the release of a large amount of heat. In the study, compounds from the BTEX group (benzene, toluene, ethylbenzene, xylenes) and PAHs (polycyclic aromatic hydrocarbons) were analyzed in the gas stream. Adsorbents used during sampling maintain their sorption properties in the temperature range of gas taken up to 50°C. Therefore, it was very important to design the suction pipeline so that the temperature of the gas taken does not exceed the permissible threshold. For this purpose the following solution was used:

a) cooling with compressed air the gas outlet connector from the metal box,
b) suction pipe length - 7 m,
c) water cooling of selected pipeline sections.

To confirm compliance with a suitably low gas temperature, constant temperature monitoring was carried out in a part of the pipeline from which gas samples were taken (Fig. 2). Ratio mouldd from the mold in a very short time, lasting about 2-3 minutes from being flooded with liquid metal. In order to avoid losses of the analyzed compounds, caused by their diffusion outside the measuring position, the gas stream flow rate through the suction pipeline of 50 ÷ 55 m^3/h had to be used. The use of such an intense gas flow through the pipeline, on the one hand, ensured that the entire stream of gases released on the test stand was directed to the pipeline, while, on the other hand, made it impossible to transport of the entire stream through the adsorbent bed. To this end, it was decided to design the system so that only part of the gas stream flowing through the pipeline could be taken at a lower speed.

The adsorbents used in the research: polyurethane foam and XAD resin (for adsorption of PAH compounds) and active carbon (for adsorption of BTEX compounds).

A pipe connector was installed in the pipeline (Fig. 4), through which gas from the stream of gases released from the mold was taken through sorption pipes at a rate of 5 l/min for PAHs and 10 l/min for BTEX, respectively.

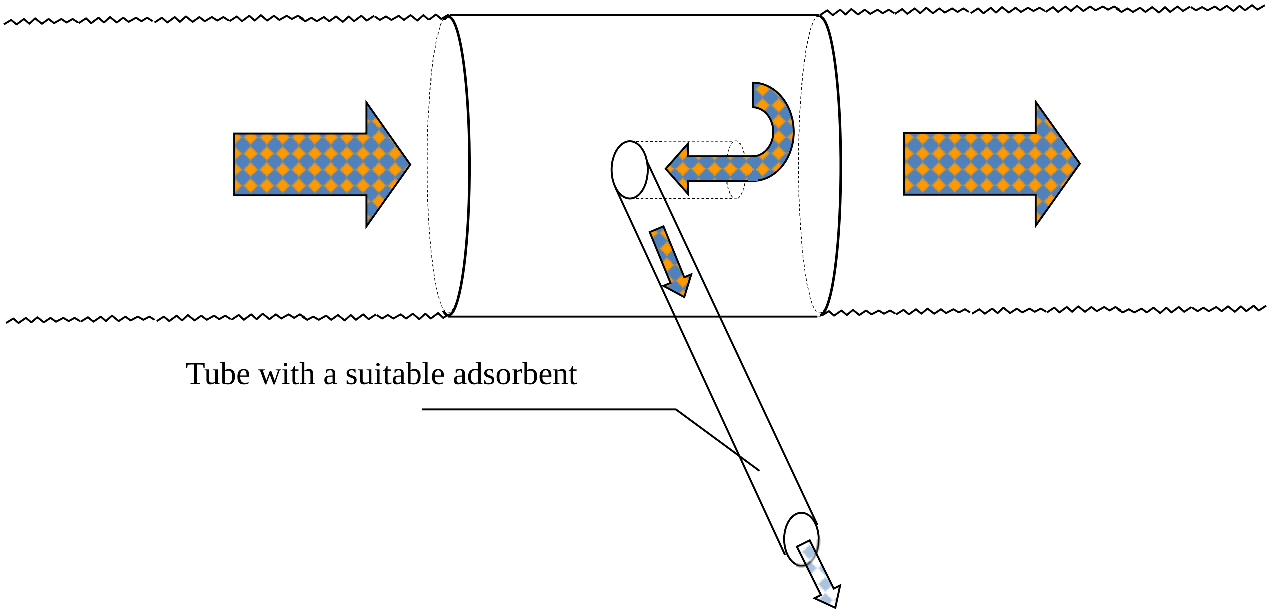

Fig. 4. Outlet connection installed in suction pipe

The composition of gases may undergo significant changes depending on the binder used for preparation of the form. For this reason, sorption tubes were designed in such a way that in the case of both low and very high concentrations of analytes in the gas stream, complete adsorption of analytes is possible. For this purpose, several layers of sorbents were placed in sorption tubes. This made it possible to assess whether the sorbent masses used in the first layers were sufficient and, at the same time, guarantee, with their possible "breakthrough", the adsorption of analytes on subsequent layers. Sorption tubes had an internal diameter of 20 mm. In tubes used for sampling PAH compounds from the gas stream, three one-gram XAD resin layers and two layers of polyurethane foam (PUF) with a height of about 40 mm were used. In tubes used to sampling BTEX compounds from the gas stream, three one-gram layers of activated carbon separated with quartz wool were used. In addition, quartz cotton wool was used as the first layer in each sorption tube to separate the dust present in the gas. The scheme of prepared tubes with sorbents is shown in Figure 5.

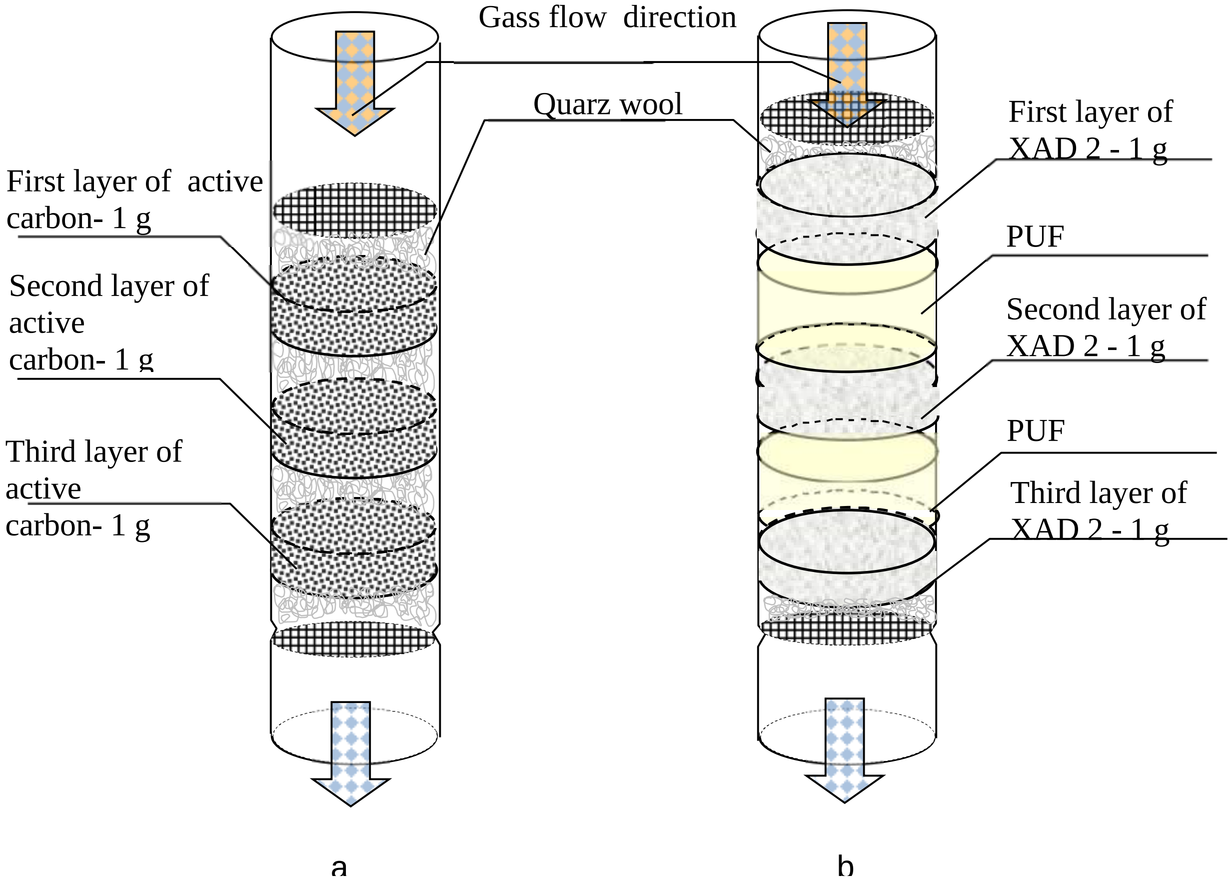

Fig. 5. Scheme of sorption tube: a) to collect compounds from the BTEX group, b) to collect compounds from the PAH group.

For the control of the analytical process, an internal control standard was added to each first layer of sorption tube just before the gas sample was taken. In the case of analysis of BTEX compounds, it was benzene d_6, while for the analysis of compounds from the PAH group, the internal standard contained: p-terphenyl d_{14}, and 2,4,6-tribromophenol.

Fig. 6 presents a part of the test stand with sorption tubes placed next to the connectors, which were used to collect gases.

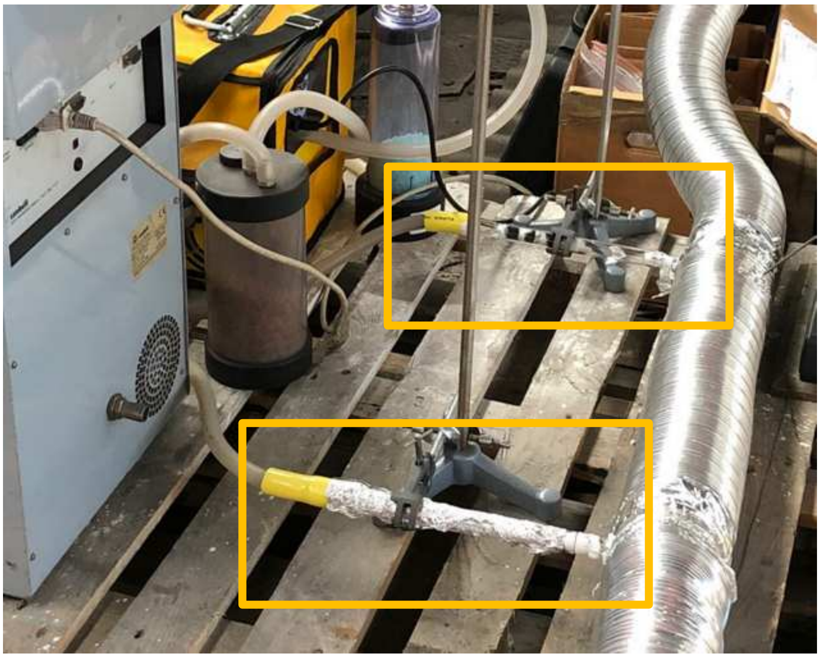

Fig. 6. Sorption tubes installed in the pipeline

Detailed informations on gas sampling parameters are presented in table 2.

Table 2. Parameters established for the gases sampling stage

Test	Gas flow rate in the pipeline [m^3/h]	Gas sampling speed [l/min]	Split of the stream	Time of sampling [min]	Comp.	Amount of adsorbent first layer/control layer [g]
1	45	5	1 : 143	30	PAH	For PAHs 3 parts of 1 g XAD 2 2 parts of PUF For BTEX 3 parts of 1 g $C_{akt\ t}$
		10	1 : 76		BTEX	
2	55	5	1 : 177		PAH	
		10	1 : 93		BTEX	
3	50	5	1 : 163		PAH	
		10	1 : 83		BTEX	
6	55	5	1 : 168		PAH	
		10	1 : 90		BTEX	
8	50	5	1:156		PAH	
		10	1:78		BTEX	
9	50	5	1:162		PAH	
		10	1:78		BTEX	

2. Determination of compounds of release gasses

2.1. Determination of compounds from the PAH group

After the gas sampling process was completed, sorption sealed tubes were stored in the refrigerator until desorption of organic compounds. For desorption of analytes, the XAD -2 adsorbent, PUF, and dust collected on quartz wool were transferred to an extraction thimble, which was placed in Soxhlet apparatus. The extraction process was carried out 4 hours. As a solvent was used 300 ml of dichloromethane. After this time, extraction was discontinued and the solution was concentrated to a volume of about 8 ml and transferred to a 10 cm^3 volumetric flask. To the extract collected in the flask, 200 µl of a standard consisting of a mixture of selected deuterated polycyclic aromatic hydrocarbons (naphthalene d$_8$, acenaphthene d$_{10}$, phenanthrene d$_{10}$, chrysene d$_{12}$, perylene d$_{12}$) was added and made up to a volume of 10 cm3. Extraction was carried out for both the first and second sorbent layers (XAD 2 + PUF). Each of the obtained extracts was analyzed by GCMS.

2.2 Determination of compounds from the BTEX group

After the gas sampling process, sorption tubes tightly packed, until desorption of organic compounds, were stored in the refrigerator. For desorption of analytes, the C_{akt} adsorbent was transferred to a sintered glass column and extraction was carried out with four portions of 10 ml diethyl ether according to the scheme shown in Figure 7.

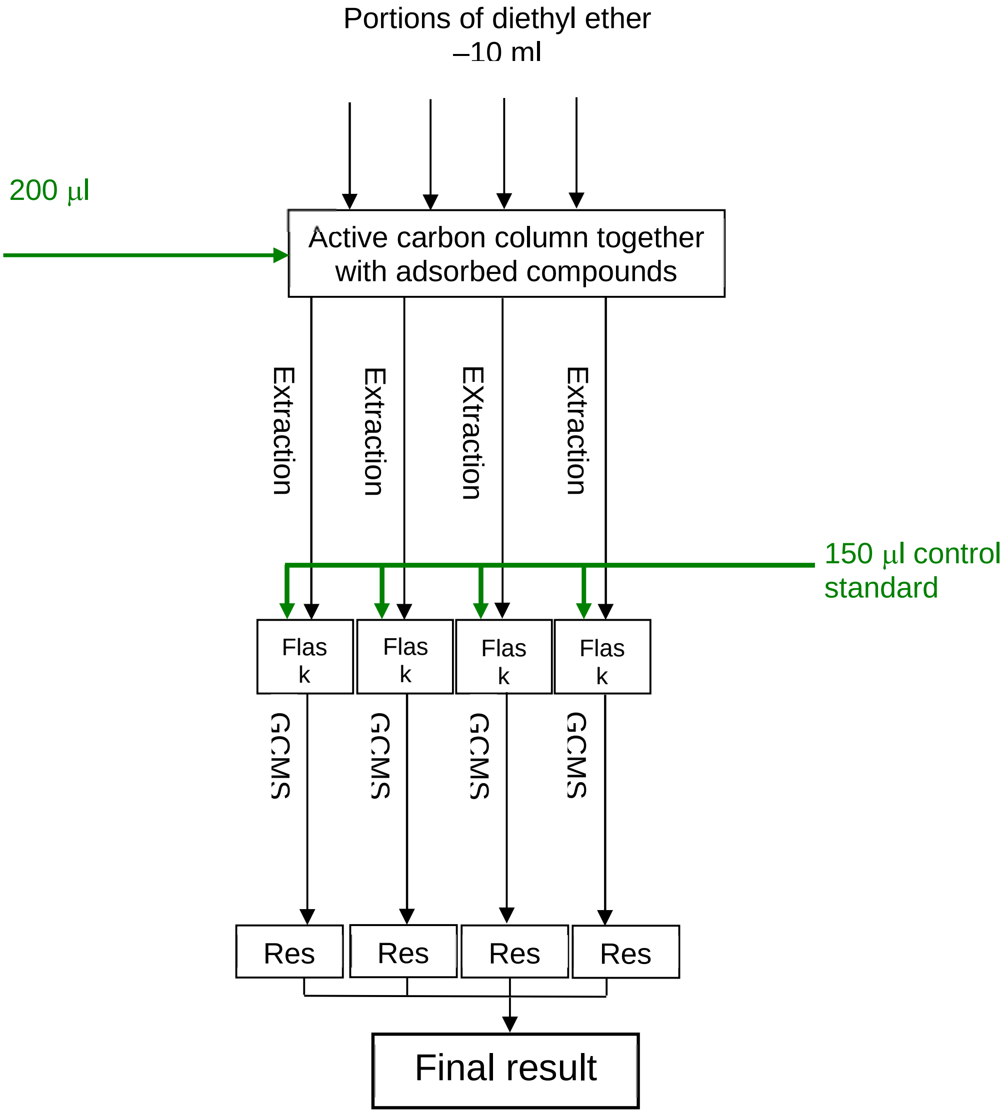

Fig. 7. Scheme of the extraction process of BTEX compounds from a single layer of activated carbon

Extraction was carried out for both the first and second active carbon layers. If a signal characteristic of BTEX compounds was observed in the second layer extract after the GCMS analysis, then the extraction of the third layer compounds was continued.

3. Gas chromatography technique combined with mass spectrometry

Identification and quantitative analysis of compounds from the BTEX and PAHs groups released during the process of pouring and cooling molds and knocking out of castings were carried out using the HRGCHRMS Finnigan MAT95X system from Thermo Electron Corporation. The components of the analyzed extracts were separated using a Trace GC Ultra gas chromatograph, equipped with a Supelco DB - 5ms capillary column, 30 m long, 0.25 mm internal diameter. The column can operate at temperatures from -60 ^{o}C to 325 ^{o}C. The Trace GC Ultra chromatograph enables operation in the range from ambient temperature (practically from about 30 ^{o}C) to 350 ^{o}C. Identification of individual components leaving the chromatographic column was carried out using a Finnigan MAT95X mass spectrometer, which acts as a detector in the measuring system. For the separation of BTEX mixtures on the chromatographic column, the gas chromatograph temperature program was used, described as *btex_ed40st_ szyb20spl63*, while for PAH determinations the program *pah-slb_5ms_spl_10_ws*. Figures 8 and 9 show chromatograms for solutions obtained after extraction of organic compounds from the first layers of adsorbents for both PAH and BTEX compounds.

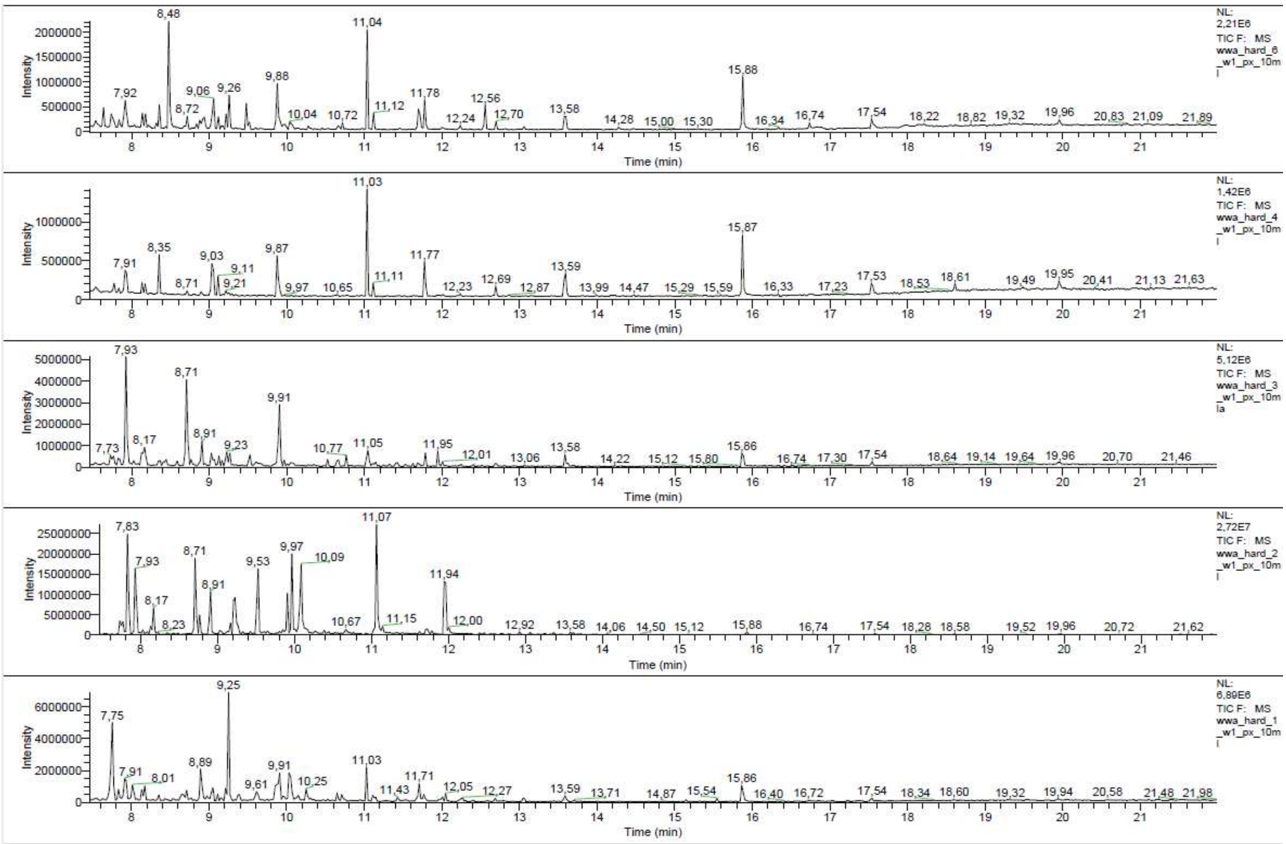

Figure 8. Chromatograms obtained for 5 extracts based on dichloromethane

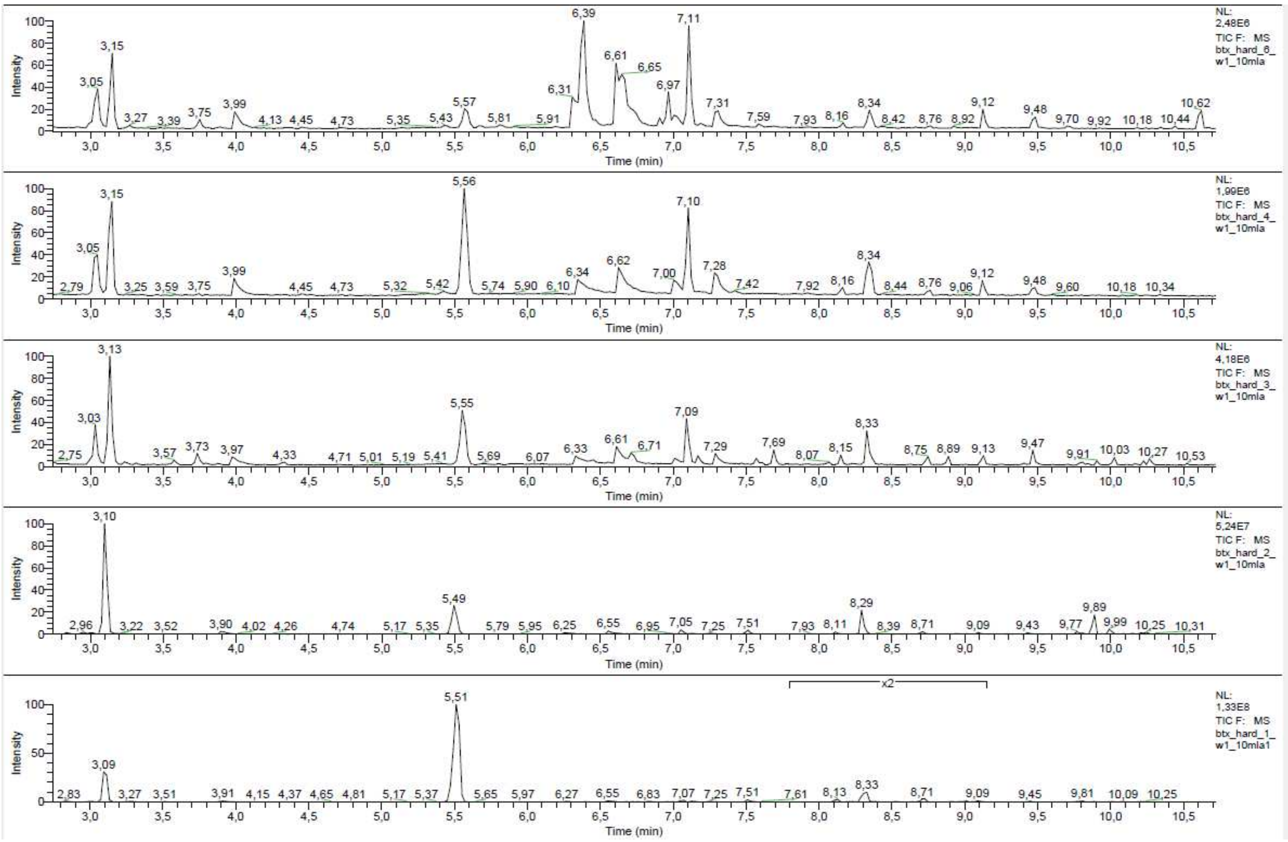

Figure 9. Chromatograms obtained for 5 extracts based on diethyl ether

4. Results

As a result of the work, information about the amount of compounds from the PAH and BTEX groups released during the pouring and cooling processes of molds and knocking out of castings was obtained. Molding sands were prepared based on 6 different binders. The obtained results are presented in Tables 3 and 4.

Table 3. Amounts of compounds from PAHs group emitted during pouring, cooling and shaking-out, *

Test	Naphthalene [mg/process]	Acenaphthylene [mg/process]	Acenaphthene [mg/process]	Fluorene [mg/process]	Phenanthrene [mg/process]	Anthracene [mg/process]	Fluoranthene [mg/process]	Pyrene [mg/process]	**SUM [mg/process]**
	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a
	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b
PAH Test 1 MF	7.7	0,1	0.2	0.5	0.7	0.4	0.2	-	**9.8**
	0.12	0.001	0.003	0.008	0.011	0.006	0.003	-	**0.15**
	0.33	0.004	0.009	0.022	0.030	0.017	0.009	-	**0.42**
PAH Test 2 MA	33	2.0	0.8	2.1	2.0	1.0	0.4	0.3	**42**
	0.51	0.031	0.012	0.032	0.031	0.015	0.006	0.005	**0.64**
	1,43	0,087	0,035	0,091	0,087	0,043	0,017	0,013	**1,8**
PAH Test 3 MB	8.3	0.7	-	0.4	0.8	0.4	0.2	0.3	**11**
	0.13	0.011	-	0.006	0.012	0.006	0.003	0.005	**0.16**
	0.36	0.030	-	0.017	0.035	0.017	0.009	0.013	**0.48**
PAH Test 6 MI	1.0	-	-	0.1	0.2	-	-	-	**1.3**
	0.015	-	-	0.001	0.003	-	-	-	**0.019**
	0.043	-	-	0.004	0.009	-	-	-	**0.056**

(a)-kg of molding sand, (b)-kg of metal

* Weight of molding sand*, kg, Weight of cast iron, kg, Content of binder % the same like in the Table 4.

Table 3. con.

Test	Naphthalene [mg/process]	Acenaphthylene [mg/process]	Acenaphthene [mg/process]	Fluorene [mg/process]	Phenanthrene [mg/process]	Anthracene [mg/process]	Fluoranthene [mg/process]	Pyrene [mg/process]	**SUM [mg/process]**
	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a	[mg/kg]^a
	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b	[mg/kg]^b
PAH Test 8 MG	4.8	0.8	3.5	0.6	0.2	0.1	0.1	0.1	**10**
	0.073	0.012	0.054	0.009	0.003	0.001	0.001	0.001	**0.15**
	0.21	0.035	0.15	0.026	0.009	0.004	0.004	0.004	**0.41**
PAH Test 9 MC	0.6	0.1	0.1	0.2	0.1	0.1	0.1	0.1	**1.4**
	0.009	0.001	0.001	0.003	0.001	0.001	0.001	0.001	**0.018**
	0.026	0.004	0.004	0.009	0.004	0.004	0.004	0.004	**0.059**

(a)-kg of molding sand, (b)-kg of metal

Table 4. Amounts of compounds from BTEX group emitted during pouring. cooling and knock-out

Test No.	Benzene [g/process]	Toluene [g/process]	Ethylbenzene [g/process]	m+p xylene [g/process]	o-xylene [g/process]	**SUM [g/process]**	**Weight of molding sand*, kg**	**Weight of cast iron, kg**	**Content of binder %**
	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]			
	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]			
BTEX Test 1 MF	1.2	4.1	0.03	0.14	0.03	**5.5**	**65***	**23**	**1.5**
	18	63	0.46	2.1	0.46	**84**			
	52	178	1.3	6.1	1.3	**238**			
BTEX Test 2 MA	1.5	0.47	0.02	0.20	0.03	**2.2**	**65***	**23**	**1.5**
	23	7.2	0.31	3.1	0.46	**34**			
	65	20	0.87	8.7	1.3	**96**			
BTEX Test 3 MB	0.17	0.11	0.01	0.03	0.01	**0.33**	**65***	**23.5**	**7**
	2.6	1.7	0.15	0.46	0.15	**5.1**			
	7.4	4.8	0.43	1.3	0.43	**14**			
BTEX Test 6 MI	0.07	0.03	0.01	0.02	0.01	**0.14**	**65***	**23.3**	**2.6**
	1.1	0.46	0.15	0.31	0.15	**2.2**			
	3.0	1.3	0.43	0.87	0.43	**6.0**			

(a)-kg of molding sand
(b)-kg of metal
Weight of molding sand* [kg] = weight of silica sand + binder

Table 4. con.

Test	Benzene [g/process]	Toluene [g/process]	Ethylbenzene [g/process]	m+p xylene [g/process]	o-xylene [g/process]	**SUM [g/process]**	**Weight of molding sand*, kg**	**Weight of cast iron, kg**	**Content of binder, %**
	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]	[mg/kg][a]			
	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]	[mg/kg][b]			
BTEX Test 8 MG	0.07	0.02	0.003	0.01	0.001	**0.11**	**69.4***	**24**	**1.8**
	1.1	0.31	0.05	0.15	0.01	**1.6**			
	3.0	0.87	0.13	0.43	0.04	**4.5**			
BTEX Test 9 MC	0.01	0.004	0.001	0.002	-	**0.02**	**68***	**24,5**	**3.3**
	0.15	0.06	0.01	0.03	-	**0.25**			
	0.43	0.17	0.04	0.09	-	**0.73**			

(a)-kg of molding sand
(b)-kg of metal
Weight of molding sand* [kg] = weight of silica sand + binder

5. Conclusions

In order to compare the harmfulness of the tested moulding sands, measurements of amounts of emitted substances from the BTEX and PAHs groups under an influence of high temperatures, were performed. Measurements were conducted for the whole cycle containing: pouring, cooling and knocking-out, within the Action B Tests in foundry plants – small scale laboratory. The obtained results were recalculated into the emission from 1 kg of the moulding sand and 1 kg of the binder applied in the given technology.

The following conclusions can be drawn on the bases of tests performed under the small scale chamber conditions:

1. Emissions of PAHs, as well as BTEX in case of moulding sands with organic binders is several dozen higher than the emission of these compounds from moulding sands with inorganic binders.

2. Green sands in respect of the PAHs emission are in the intermediate sphere, while in respect of the BTEX emission are comparable with moulding sands with inorganic binders.

3. From the comparison of moulding sands with organic binders it results, that the BTEX emission from the MA sand is more than two times lower than the emission from the MF sand, while benzene and toluene predominate in the composition of gases emitted from both sands.

4. Moulding sands with inorganic binders are comparable in terms of the emission amount of substances from the BTEX and PAHs groups. Higher values of the unitary emission from moulding sands with MG binder are the result of using the organic liquid hardener for this binder hardening, while for the hardening of the remaining two binders (MI, MC) high temperatures were used.

5. Moulding sands with inorganic binders (MG, MC and MI) are characterised by lower harmfulness for the environment and employees than moulding sands with organic binders.

6. Relatively environment friendly were green sands (MB), in which a part of coal dust was substituted by additions able to produce lustrous carbon.