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TG/DTG/DTA, FTIR and GC/MS Studies of Oil Sand for Artistic and Precision Foundry with the Emission of Gases Assessment

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Abstract

The paper presents the results of thermoanalytical studies by TG/DTG/DTA, FTIR and GC/MS for the oil sand used in art and precision foundry. On the basis of course of DTG and DTA curves the characteristic temperature points for thermal effects accompanying the thermal decomposition reactions were determined. This results were linked with structural changes occurred in sample. It has been shown that the highest weight loss of the sample at temperatures of about 320°C is associated with destruction of C-H bonds (FTIR). In addition, a large volume of gases and high amounts of compounds from the BTEX group are generated when liquid metal interacts with oil sand. The results show, that compared to other molding sands used in foundry, this material is characterized by the highest gaseous emissions and the highest harmfulness, because benzene emissions per kilogram of oil sand are more than 7 times higher than molding sand with furan and phenolic binders and green sand with bentonite and lustrous carbon carrier.

Keywords: Molding sand, Thermal analysis, Emission of gases, FTIR, GC/MS

1. Introduction

The interaction of liquid metal with molding sand leads to many physicochemical changes. Their effect among others, is thermal destruction of the binder, which causes the emission of gases [1-12]. The composition of this gases and its harmfulness depends on many factors, mainly on the binder type (resin, hardener), molding sand composition (amount of binder, reclaim participation), contact time with high temperature to knocking out casting from mold [13, 14]. This information can be helpful during planning of reclamation treatments of waste molding sands, because they allow to choose the correct temperature of thermal reclamation processes, which can be very important in energy management in foundry [15-19].

The assessment of molding sands in range of its harmfulness to the environment and working conditions for employees in the foundry industry is made by the determination of emissions of compounds from BTEX group (benzene, toluene, ethylbenzene, xylenes) and PAH's (polycyclic aromatic hydrocarbons), which are considered as an indicator of the harmfulness of molding and core sands. The total volume of gases generated during the thermal destruction of the binder is also important, because it can influence on the formation of defects in castings [20-31].

The aim of this work was the assessment of temperature influence on changes in the oil sand, designed for artistic and precision casting, in terms of structural changes and BTEX compounds emission.

For many years, the assessment of the harmfulness of foundry molding sands has been the subject of studies conducted by researchers from Faculty od Foundry Engineering -AGH.

2. Materials for research

The investigation were conducted for oil sand mixture consists of fine silica sand grains and oil binder. The molding sand was delivered by manufacturer as a product ready for use. The safety data sheet does not specify the diameter of the sand grains or qualitative and quantitative composition of molding sand (e.g. the type and proportion of binder and other additives). Characteristic for this material is no drying effect and ability to rebonding (refreshing) of its properties by adding a sufficient amount of fresh additives. It is designed for making molds for thin-walled castings, of which require high dimensional accuracy. Similarly to the other molding sands with a high degree of grain matrix dispersion, this material is characterised by low permeability, which should be taken into account during preparation of casting molds (by planning suitable amount of vents).

3. Research methodology

In the first step of research, sample of oil sand was subjected to the thermal analysis. Test was performed by using Thermal Analyzer produced by Jota. The temperature range of test was 20-1000°C and a heating rate was of 10°C/min., in oxygen atmosphere. Obtained results, mainly characteristic temperature points, were important information for planning structural studies by FTIR transmission technique, which were conducted in the conditions corresponding to occurrence heating effects on TG/DTA curves. Preparation of the samples for studies consisted in heating of material in a laboratory oven at the same heating rate as during of the thermal analysis (10°C/min). At the next stage, investigation of gas emission at the test stand developed at the Faculty of Foundry Engineering AGH [32] (Fig. 1) was carried out.

A molding sand sample, of known mass was placed in a steel tube (special designed holder). Tube with molding sand was placed in the cavity of the mold in such a way to ensure contact the entire surface of sample with the liquid metal. The mold was pouring with cast iron at 1350°C. Gas samples for GC-MS analysis were collected on activated coal bed, which was then extracted with dimethyl ether. The research was aimed at determining the total volume of gases and amounts of BTEX compounds generated from sample.

4. Research results and their analysis

Figure 2 and 3 shows curves of the TG/DTG/DTA recorded in the temperature range of 25-1000°C for a sample of the oil sand.

TG/DTG/DTA curves indicated the occurrence of the endothermic effect of heat at a temperature of about 90°C combined with a low weight loss. In a further step of sample heating, reactions with heat releasing were observed in the range of 200-400°C, with a maximum of changes at 330°C, accompanied by the largest loss of mass. A second weight loss of 450-750°C on the DTG curve was also recorded with a maximum of changes at temperature about 520°C. It is connected with a small endothermic effect. The total weight loss of the sample is 4.92%, which indicates that the total content of the oil binder in the molding sand was about 5 parts by mass.

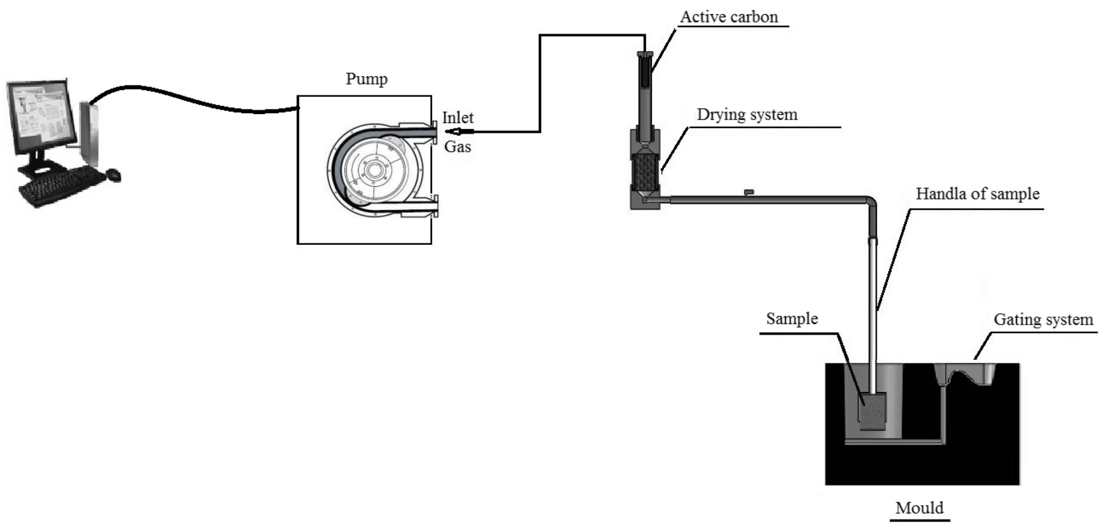

Fig. 1. Station for research of the volume and harmfulness of gases compounds emitted from the materials used in foundry and metallurgical processes [33]

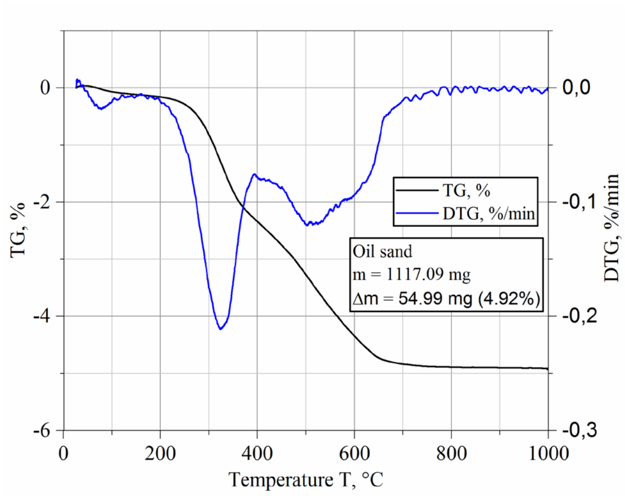

Fig. 2. TG/DTG curves for a sample of the oil sand

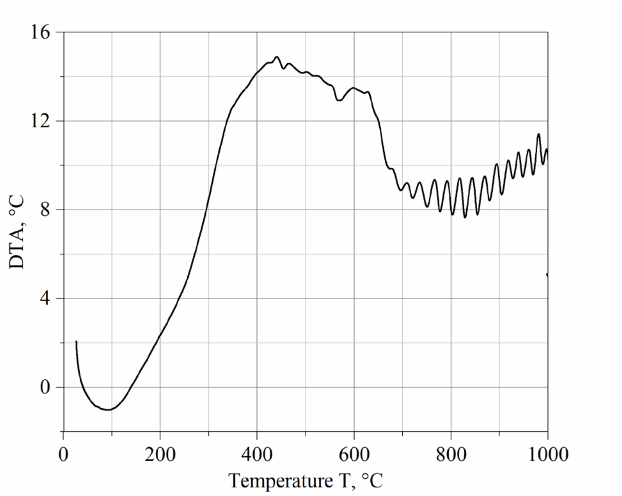

Fig. 3. DTA curve for a sample of the oil sand

Figure 4 shows the IR spectrum of the oil sand at the initial state and spectra of molding sand after heating at the characteristic points determined by the thermal analysis.

IR spectra of oil sand the characteristic bands for quartz sand (1043, 777, 691, 520, 460 cm^{-1}) were noticed. The occurrence of bands at wave number 2924 cm^{-1} and 2853 cm^{-1} was indicated the presence of C-H vibration from organic additives. The bands characteristic for organic compounds were indicated also in the range 2000-1450 cm^{-1}. At a temperature of about 70°C was observed weaken the intensity of band 3429 cm^{-1}, which may be associated with an endothermic heat effect on the DTA curve and a few percentage weight loss (DTG curve) associated with evaporation of water. At a temperature of 320°C was noticed the greatest loss of weight, which was evidence of thermal degradation of organic additives and was confirmed in the obtained IR spectrum (Fig. 4, spectrum c). At this temperature, the vibrations of C-H (2924 and 2853 cm^{-1}) and the deformation band at 1466 cm^{-1} have disappeared.

This was an exothermic reaction which occurs to a temperature of 450°C. In addition, the difference in the half-width of the main band at 1043 cm^{-1} can be indicated This change, which was observed further in the higher temperature accompanied also with intensity weakening of the band at 520 cm^{-1} and the change of intensity ratio of 1043 cm^{-1} to 777 cm^{-1}– and 690 cm^{-1}. This change can be combined with the polymorphic transformation of β-quartz into α-quartz. At about 560°C a endothermic thermal effect was recorded, which can be bound possibly from dehydroxylation of the binder components. This is evidenced by the disappearance band with maximum at 3623 cm^{-1} (Fig. 4, spectrum e).

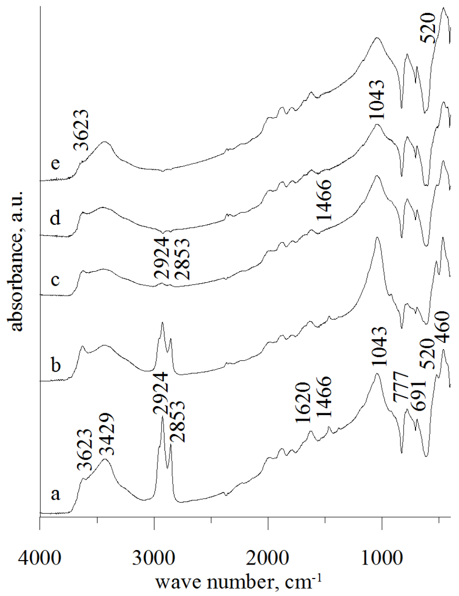

Fig. 4. IR spectra of the oil sand treated at temperature (a - 20°C, b - 70°C, c - 320°C, d - 450°C, e - 560°C)

The study involved also chromatographic analysis of selected thermal decomposition products (mainly aromatic hydrocarbons from BTEX group, it means benzene, toluene, ethylbenzene, xylenes) of oil sand for artistic and precision foundry.

Measurement methodology was developed based on literature review and own research [34-40].

Substances were extracted from adsorption columns by means of diethyl ether. Products of pyrolysis were separated on a Rxi-5Sil MS column (30 m length, 0.25 mm diameter). Helium (flow: 1 ml/min) was used as a carrier gas. The column was installed in a Focus gas chromatograph (Thermo Scientific, USA). In the research, a temperature program used for analysis was applied: an initial temperature of 40°C was held for 2 min; ramped 10°C/min and up to 150°C, and then 150°C was maintained for 10 min. Chromatograms were recorded by a ISQ (Thermo Scientific, USA) single quadrupole mass spectrometer in the range 30-400 m/z. Electron ionisation (EI) at a temperature of 250°C was applied, electron energy - 70 eV.

Table 1 shows results of gases emission from oil sand, in terms of overall emissions of gases during pouring of molten metal and emission of compounds from BTEX group.

Table 1.
Emissions of BTEX compounds from the oil sand (mg/kg molding sand)

Mass of sample,g	Volume of gases, dm^3/ kg	Emissions of gases, mg/kg			
		B	T	E	X
40	112.10	2646.22	61.05	4.87	22.15

Table 2 gives a summary of the emissions for different types of molding sands. It was prepared on the basis of results of the author's own studies and data available in the literature.

Table 2.
Comparison of gas emission and amount compounds from BTEX group from molding sands with different binders [33, 41, 42]

Molding sand type	Volume of gases, dm^3/kg	Emissions of gases, mg/kg			
		B	T	E	X
1	112.100	2646.22	61.05	4.87	22.15
2	19.110	386.73	9.76	0.13	1.19
3	17.373	325.89	29.33	0.22	1.86
4	9.909	37.00	0.58	0.01	0.00

Explanation of a shortcuts:
1 - oil molding sand (total content of binder about 5 parts by mass);
2 - green sand with bentonite (content of bentonite-lustrous carbon carrier mixture about 8 parts by mass - the sample in the dry state);
3 - molding sand with phenol resin (total content of binder about 1.5 parts by mass);
4 - molding sand with geopolymer binder system (total content of binder about 2.2 parts by mass).

Table 3.
Comparison of amount compounds from BTEX group converted into 1 part by mass of the binder

Binder type	Emissions of gases, mg/1 part of mass			
	B	T	E	X
1	529.24	12.21	0.97	4.43
2	48.34	1.22	0.01	0.15
3	217.26	19.55	0.15	1.24
4	16.82	0.26	0.00	0.00

Pouring molten metal into mold prepared on basis of oil sand was associated with higher gas emissions compared to other types of molding sands. In result of the decomposition of binder, from this molding sand were emitted approx. 5 times more gases than from the popular green sand with bentonite and nearly 10 times more gases than from molding sand with geopolymer binders. The use of fine-grained matrix required the introduction of more binder, due to the high surface development and caused much higher gaseous emissions. However, this molding sand apart from the high emissivity of gases, was also highly harmful. Oil sand emitted a large amount of benzene to the environment (per 1 kg of molding sand) - approx. 7 times more than the green sands and molding sands bonded by phenolic binder.

After conversion into 1 part of mass of binder emission of benzene from oil binder is more than 11 times higher that of the bentonite with carbon carrier mixtures and more than 2 times higher than phenolic resin. Compared to geopolymer binder the oil binder emitted more than 30 times higher harmful benzene.

The studies discussed in this paper presents measurements for an extremely unfavourable case. The entire volume of the sample was gasified, which does not occur in real condition in the mold. However, this molding sand type is intended for artistic and precision casting, where casting process is carried out of alloys at a lower temperature (e.g. aluminium alloys) and gas emissions will be significantly lower. Reducing emissions can also favour the rapid removal of castings from the mold to limiting the thermal impact of the liquid metal with molding sand.

Figures 5 and 6 illustrate the volume and kinetics of gas emissions from oil sand during liquid metal pouring.

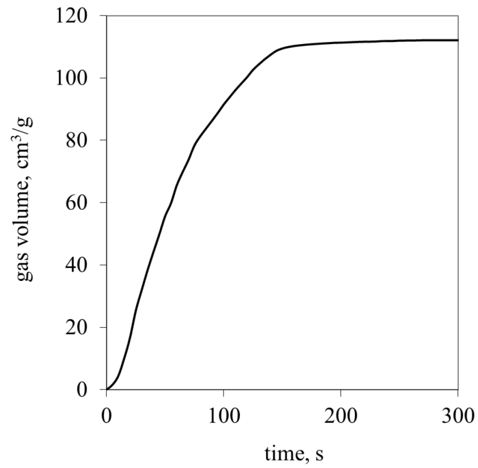

Fig. 5. Volume of gases emitted during pouring molds based on oil sand

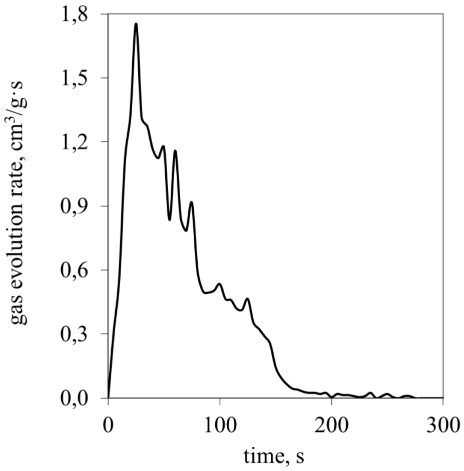

Fig. 6. The emission rate of gases from the oil sand

5. Conclusions

Based on the obtained results, the following conclusions can be drawn:

- The thermal analysis of the oil sand allows the indicate of three characteristic temperature points accompanied by a loss of weight. The first one was probably related to the loss of adsorbed water, the second one to the decomposition of C-H bonds, and the third to dehydration (and phase change) as confirmed by structural studies by FTIR.
- The highest gas emission rate was recorded approximately 30 seconds after pouring molten metal and was about 1,8 $cm^3/g \cdot s$. The total volume of generated gases was approximately 122 dm^3/kg.
- Compared to other molding sands used in foundry, this material is characterized by the highest gaseous emissions and the highest harmfulness, because benzene emissions per kilogram of oil sand are more than 7 times higher than molding sand with furan and phenolic binders and green sand with bentonite and lustrous carbon carrier.
- The research results discussed in this paper present an extremely unfavourable case when the entire volume of sample is gasified. So the situation in the real conditions in the foundry does not occur.
- The sample based on oil sand was pouring with liquid cast iron at 1350°C, because it made it possible to compare the harmfulness of emitted gases with results obtained for other types of molding sands in the same conditions (Table 2). It should be expected that during the casting of alloys with lower melting temperature (for example, aluminum alloys, where the pouring temperature, depending on the composition of the alloy, is about 700-800°C) the level of gases emission will be significantly lower.

Acknowledgements

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References

[1] McKinley, M.D., Lytle, C.A. & Bertsch, W. (1999). Pyrolysis of core resins used in Metalcasting. *AFS Transactions.* 107, 407-412.

[2] Liang, J.J. & Tsay, G.S. (2010). Composition and yield of the pernicious and stench gases in furan sand model founding process. *Sustainable Environment Research.* 20(2), 115-125.

[3] Grabowska, B., Kaczmarska, K., Bobrowski, A., Żymankowska-Kumon, S. & Kurleto-Kozioł, Ż. (2017). TG-DTG-DSC, FTIR, DRIFT and Py-GC-MS studies of thermal decomposition for poly(sodium acrylate)/dextrin (PAANa/D) – new binder BioCo3. *Journal of Casting&Materials Engineering.* 1(1), 27-32.

[4] Grabowska, B., Malinowski, P. Szucki M. & Byczyński, Ł. (2016). Thermal analysis in foundry technology. Pt. 1, Study TG-DSC of the new class of polymer binders BioCo. *Journal of Thermal Analysis and Calorimetry.* 126(1), 245-250.

[5] Acharya, S.G., Vadher, J.A. & Kanjariya, P.V. (2016). Identification and Quantification of Gases Releasing From Furan No Bake Binder. *Archives of Foundry Engineering.* 16(3), 5-10.

[6] Tiedje, N., Crepaz, R., Eggert, T. & Bey, N. (2010). Emission of organic compounds from mould and core binders used for casting iron, aluminium and bronze in sand moulds. *Journal of Environmental Science and Health Part A.* 45, 1866-1876.

[7] Zhang, H., Zhao, H., Zheng, K., Li, X., Liu, G. & Wan, Y. (2014). Diminishing hazardous air pollutant emissions from pyrolysis of furan no-bake binders using methanesulfonic acid as the binder catalyst. *Journal of Thermal Analysis and Calorimetry*. 116, 373-381.

[8] Samuels, G., Beckermann, C. (2011). Measurement of Gas Evolution from PUNB Bonded Sand as a Function of Temperature. 65th SFSA Technical and Operating Conference, Steel Foundries Society of America, Chicago. Paper No 5.6.

[9] Zhang, B., Garro, M., Chautard, D. & Tagliano, C. (2002). Gas Evolution from Resin-Bonded Sand Cores Prepared by Various Processes. *Metallurgical Science and Technology.* 20(2), 27-32.

[10] Giese, S.R., Roorda, S.C., & Patterson, M.A. (2009). Thermal Analysis of Phenolic Urethane Binder and Correlated Properties. *AFS Transactions.* 117, 355-366.

[11] Grefhorst, C., Senden, W., Ilman, R., Podobed, O., Lafay, V. & Tilch, W. (2010). Reduction of greensand emissions by minimum 25% - case study. *China Foundry.* 7(4), 419-424.

[12] Abedghars, M.T., Hadji, A. & Bouhouch, S. (2011). Monotoring of air quality in an iron foundry (Case of NO_x, SO_2, benzene and dust). *J. Mater. Environ. Sci.* 2(1), 501-506.

[13] Kaczmarska, K., Bobrowski, A., Żymankowska-Kumon, S. & Grabowska, B. (2017). Studies on the gases emission under high temperature condition from moulding sands bonded by modified starch CMS-Na. *Archives of Foundry Engineering.* 17(1), 79-82.

[14] Żymankowska-Kumon, S., Bobrowski, A. & Grabowska, B. (2016). Comparison of the emission of aromatic hydrocarbons from moulding sands with furfural resin with the low content of furfuryl alcohol and different activators. *Archives of Foundry Engineering.* 16(4), 187-190.

[15] Łucarz, M. (2015). Setting temperature for thermal reclamation of used moulding sands on the basis of thermal analysis. *Metalurgija.* 54(2), 319-322.

[16] Łucarz, M. (2015). Thermal reclamation of the used moulding sands. *Metalurgija.* 54(1), 109-112.

[17] Dańko, R. (2013). Criteria for an advanced assessment of quality of moulding sands with organic binders and reclamation process products. *China Foundry.* 10(3), 181-186.

[18] Energy and Environmental Profile of the U.S. Metalcasting Industry Prepared by Energetics, Incorporated Prepared for U.S. Department of Energy Office of Industrial Technologies, September 1999. (https://energy.gov/sites/prod/files/2013/11/f4/profile_0.pdf)

[19] Łucarz, M. (2014). *The effect of mechanical and thermal reclamation on the matrix of quartz grain state*. Kraków, Wydawnictwo Naukowe „AKAPIT".

[20] Bates, C.E. & Scott, W.D. (1975). Decomposition of resin binders and the relationship between the gases formed and the casting surface quality – part 1. *AFS Transactions.* 83, 519-524.

[21] Bates, C.E. & Scott, W.D. (1976). Decomposition of resin binders and the relationship between the gases formed and the casting surface quality – part 1. *AFS Transactions.* 84, 793-803.

[22] Bates, C.E. & Scott W.D. (1977). Decomposition of resin binders and the relationship between the gases formed and the casting surface quality – part 1. *AFS Transactions.* 85, 209-226.

[23] Kubecki, M. & Holtzer, M. (2016). Evaluation of the influence of the reclaimed addition on the amount of compounds from BTEX group, generated during pouring molten metal into the form. *Prace Instytutu Metalurgii Żelaza.* 67(4), 20-23.

[24] Bates, C.E., & Burch, R. (2007). Core and Mold Gas Evolution: Porosity in Castings, *Foundry Management & Technology*. 135(5), 17-18.

[25] Naro, R.L. (1999). Porosity Defects in Iron Castings from Mold-Metal Interface Reactions. *AFS Transactions.* 107, 839-851.

[26] Monroe, R. (2005). Porosity in Castings. *AFS Transactions.* 113, 519-546.

[27] Winardi, L., Littleton, H.E. & Bates, C.E. (2007). Gas Pressures in Sand Cores. *AFS Transactions.* 115, 303-312.

[28] Scraber, P., Bates C. & Griffin J. (2006). Avoiding gas defects through mold and core package design. *Modern Casting.* 96(12), 38-40.

[29] Totten, G.E., Funatani, K., Xie, L. (2004). *Handbook of Metallurgical Process Design*. Marcel Dekker Inc. New York.

[30] Wang, Y., Zhang, Y., Su, L., Li, X., Duan, L., Wang, C. & Huang, T. (2011). Hazardous air pollutant formation pyrolysis of typical Chinese casting materials. *Environ. Sci. Technol.* 45(15), 6539-6544. DOI: 10.1021/es200310p.

[31] Zhao, X., Ning, Z., Li, Z., Zou, W., Li B., Huang Y., Cao F., Sun J. (2017). Evolved gas analysis of PEP-SET sand by TG and FTIR. *Journal of Analytical and Applied Pyrolysis.* (in press). https://doi.org/10.1016/j.jaap.2017.04.012.

[32] Holtzer, M., Dańko, J., Lewandowski, J.L., Solarski, W., Dańko, R., Grabowska, B., Bobrowski, A., Żymankowska-Kumon, S., Sroczyński, A., Różycki, A. & Skrzyński, M. (2017). Station for research of the volume and harmfulness of gases compounds from the materials used in foundry and metallurgical processes. Polish patent. PL 224705 B1.

[33] Bobrowski, A., Holtzer, M., Żymankowska-Kumon, S. & Dańko, R. (2015). Harmfulness assessment of moulding sands with a geopolymer binder and a new hardener, in an aspect of the emission of substances from the BTEX group. *Archives of Metallurgy and Materials*. 60(1), 341-344.

[34] Makhathinia, T.P. & Rathilalb, S. (2017). Investigation of BTEX compounds adsorption onto polystyrenic resin. *South African Journal of Chemical Engineering.* 23, 71-80. https://doi.org/10.1016/j.sajce.2017.03.001.

[35] Fabbri, D. & Vassura, I. (2006). Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis. *Journal of Analysis and Applied Pyrolysis.* 75, 150-158. https://doi.org/10.1016/j.jaap.2005.05.003.

[36] Cacho, J.I., Campillo, N., Viñas, P. & Hernández-Córdoba, M. (2016). Gas chromatography-mass spectrometry using microvial insert thermal desorption for the determination of BTEX in edible oils. *RSC Advances.* 6(25), 20886-20891.

[37] Milczarek, J.M. & Zięba-Palus, J. (2009). Examination of spray paints on plasters by the use of pyrolysis-gas chromatography/mass spectrometry for forensic purposes. *Journal of Analytical and Applied Pyrolysis.* 86(2), 252-259.

[38] Durmusoglu, E., Taspinar, F. & Karademir, A. (2010). Health risk assessment of BTEX emissions in the landfill environment. *Journal of Hazardous Materials.* 176, 870-877.

[39] Grygierczyk, G. (2016). Chromatographic analysis of organic compounds on impregnated chemically bonded stationary phases. part 1. *Acta chromatographica.* 17, 302-313.

[40] Acharya, S.G., Vadher, J.A. & Kanjariya, P.V. (2016). Identification and Quantification of Gases Releasing From Furan No Bake Binder. *Archives of Foundry Engineering.* 16(3), 5-10.

[41] Holtzer, M., Grabowska, B., Żymankowska-Kumon, S., Kwaśniewska-Królikowska, D., Dańko, R., Solarski, W. & Bobrowski, A. (2012). Harmfulness of moulding sands with bentonite and lustrous carbon carriers. *Metalurgija.* 51(4), 437-440.

[42] Bobrowski, A., Holtzer, M., Dańko, R. & Żymankowska – Kumon, S. (2013). Analysis of gases emitted during a thermal decomposition of the selected phenolic binders. *Metalurgia International.* 18(7), 259-261.