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Ecological assessment of foundry binders from cold-box technology by gas chromatography method

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ABSTRACT

Casting is a technique for preparing metal products of a predetermined shape and properties. This technique involves filling with liquid metal alloys the casting moulds, which mapped the required product, eg. motor housing. Archaeological studies show that already in the Stone Age man used in his everyday life, some metallic materials - much earlier, before discovering their metallurgical properties. Castings are necessary in every area of the economy. Unfortunately, during the foundry process workers are exposed to various harmful agents, including the emission of hazardous substances. One of emission sources are foundry binders, used for production of moulding sands and cores, which at high temperature thermally decompose. Depending on the type of binder and the temperature and exposition time, can be formed compounds such as furfuryl alcohol, formaldehyde, phenol, aromatic hydrocarbons from the BTEX group (benzene, toluene, ethylbenzene, xylenes) and others. For the analysis of these compounds the most efficient technique is gas chromatography method coupled with mass spectrometry (GC/MS). The advantage of this method is, among others, its high sensitivity due to which very small samples of the analysed substances can be used – from 0,1 μl. The subject of investigations was the ecological assessment of binder based on phenol-urethane resin, where the catalyst (hardener) was an amine. This binder is used in cold-box technology to produce foundry cores.

***Keywords*:** foundry, binder, resin, cores, gas chromatography, mass spectrometry

1. INTRODUCTION

Foundry is a process that produces metal castings. Metals are cast into shapes by melting them into a liquid, pouring the metal in a mould, and removing the mould material or casting after the metal has solidified as it cools. The most popular metals processed are aluminium and cast iron. However, other metals, such as bronze, steel and others, are also used to produce castings in many foundries. In this process, parts of desired shapes and sizes can be formed (SWA, 2013; NOH&SC, 1989).

Foundry has been identified as a dangerous area because:

- large numbers of workers are exposed to chemicals and substances we know can cause long latency disease (eg. chemical binder, solvents, benzene);
- there is a very high incidence of long latency disease (SWA, 2013).

During casting processes comes to emission of harmful gases, mainly volatile organic compounds (VOCs). This is a particularly important problem for the foundry, because these gases can endanger the environment. Compounds (Fig. 1) from harmful gases are the cause of many occupational diseases (Holtzer et al., 2013; Szymański et al., 2012). These occurrence are caused by the use for production of moulding sand and cores for example organic resins.

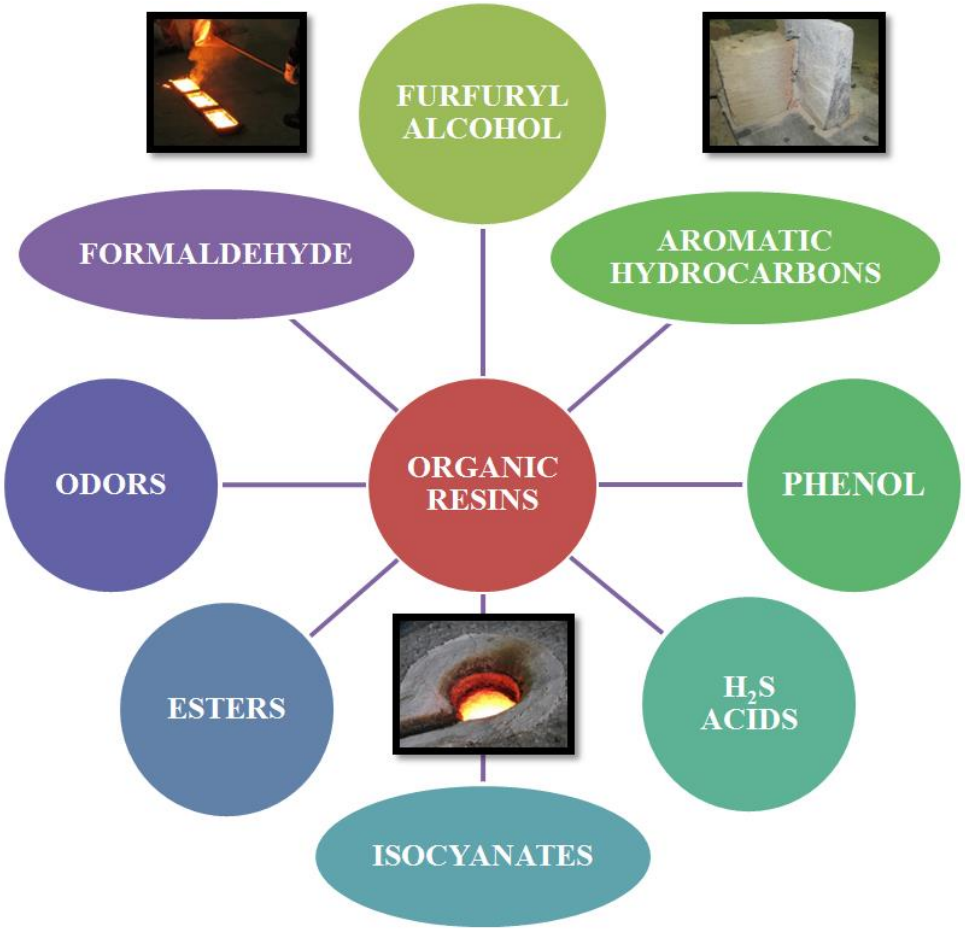

Figure 1. Pollution emitted into the atmosphere during the foundry process of preparing selected moulding sands with binders based on organic resins.

In the production of foundry cores, the most popular is method of cold-box with phenol-urethane resin and amine catalyst. This method has a number of advantages but the cores made from cold-box have a high gases emission (Blackledge, 1981; Fabbri & Vassura, 2006).

The identification of aromatic hydrocarbons produced during the thermal decomposition of foundry binders is helpful chromatographic analysis. Typical uses of gas chromatography (GC) include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined).

In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column (Żymankowska-Kumon, 2015). The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness (Zięba-Palus et al., 2008).

The combination of a gas chromatograph and mass spectrometer (GC/MS) is used primarily to identify of organic compounds. Applications of GC/MS (Fig. 2) include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification. GC-MS has been widely heralded as a standard for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample. A non-specific test merely indicates that a substance falls into a category of substances (Palmer & Scott, 1981). Although a non-specific test could statistically suggest the identity of the substance, this could lead to false positive identification (Kubecki, 2010). The main advantages of GC/MS method include the ability to simulta-neously separation, identification and quantitative analysis of the test compounds. You can detect even small amounts of organic compounds due to the very high sensitivity of detection. The gas chromatograph is then treated as a sample insertion system (Fox et al., 2002).

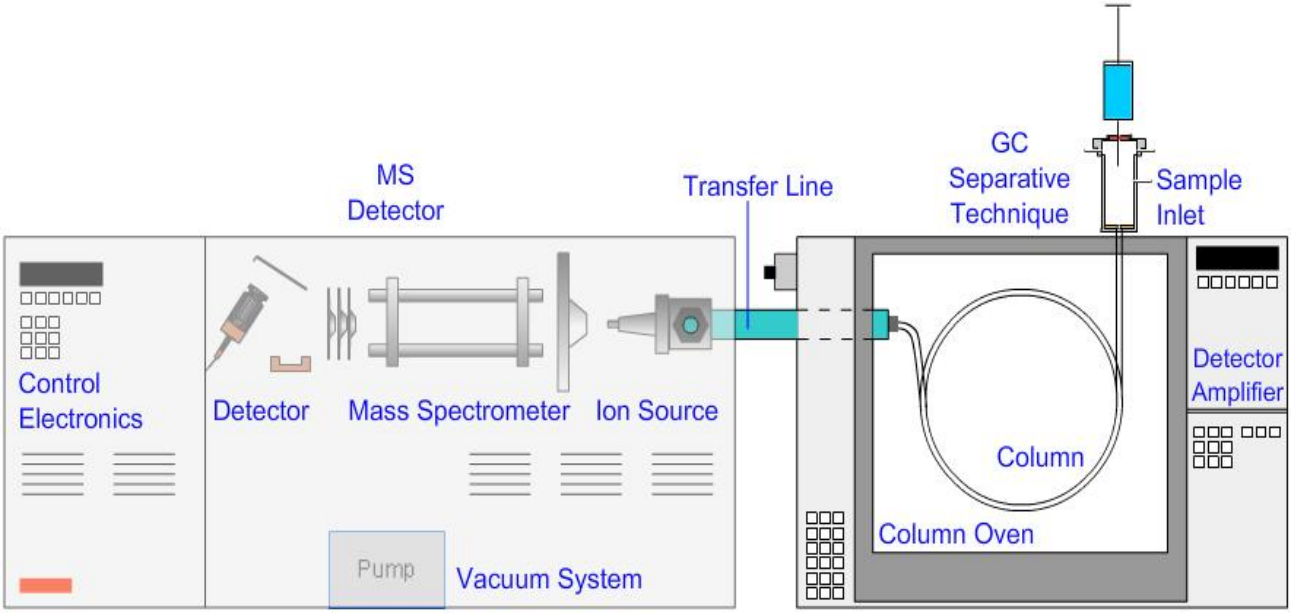

Figure 2. Schematic of a typical bench top GC-MS system (Chromacademy, 2016).

In case of the pyrolysis gas chromatography (Py-GC/MS) method is based on transforming a solid sample into gas by heating the sample in an atmosphere of inert gas (helium) in a pyrolyser (Py), which is accompanied by thermal decomposition (Lachowicz et al., 2012; Milczarek et al., 2009 a). The sample is put into direct contact with a platinum wire, or placed in a quartz sample tube, and rapidly heated to set temperature (e.g. up to 1400 °C). Three different heating techniques are used in actual pyrolysers: isothermal furnace, inductive heating (Curie Point filament), and resistive heating using platinum filaments (method from this article). Large molecules cleave at their weakest points and produce smaller, more volatile fragments (Milczarek et al., 2009 b). These fragments are separated on a chromatographic column in a chromatograph. The separated compounds are analysed in a mass spectrometer.

2. MATERIALS AND METHODS

The study involved a chromatographic analysis (Fig. 3) of selected thermal decomposition products (mainly aromatic hydrocarbons, especially benzene) of foundry binder used to preparation of cores. The binder based on phenol-urethane resin and amine catalyst.

Range temperature of thermal decomposition: 500, 900 and 1100 °C. A Pyroprobe 5000 pyrolyser (CDS Analytical, USA) was used in the performed research. It has a platinum coil, which enables heating of a sample to any temperature within the range 1-1400 °C at a rate of up to 999,9 °C/s. Products of pyrolysis were separated on a TR-SQC tested 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 of aromatic hydrocarbons was applied (Żymankowska-Kumon, 2015): 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.

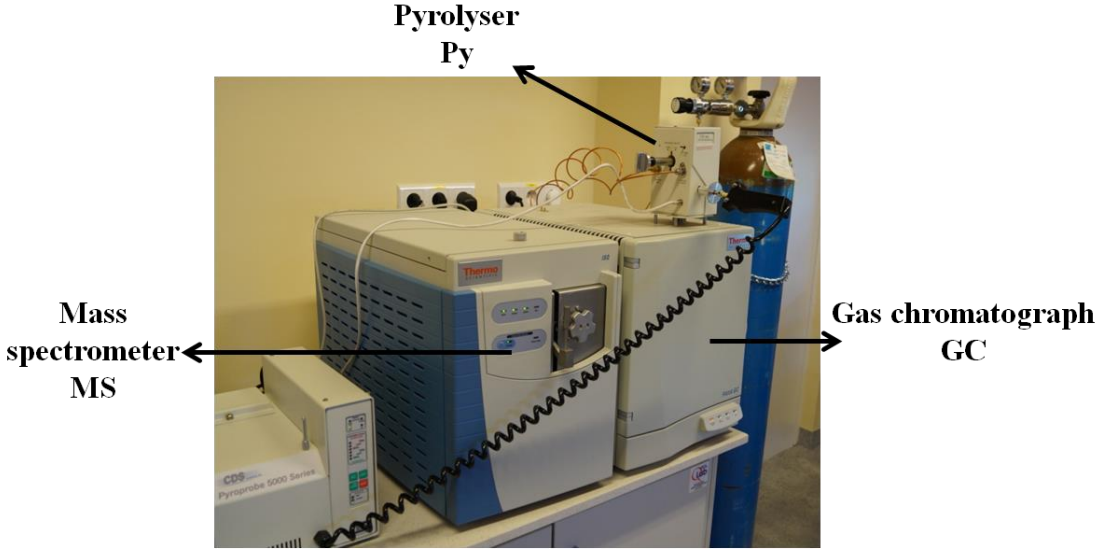

Figure 3. Measuring station for chromatographic analysis (Py-GC/MS method).

3. RESULTS

Chromatograms of tested samples are presented in Figure 4; they were obtained after pyrolysis at temperatures of 500, 900 and 1100 °C. The results of analysis of main components (identification) are presented in Table 1.

Table 1. Results of Py-GC/MS analysis

Compound name	Numer CAS	Temperature, °C					
		500		900		1100	
		R_T, min	P, %	R_T, min	P, %	R_T, min	P, %
Benzene	71-43-2	1,45	72,04	1,14	87,62	1,44	91,45
Toluene	108-88-3	4,80	84,15	3,51	79,97	3,55	61,87
Ethylbenzene	100-41-4	6,61	76,27	7,12	86,58	6,34	58,43
m-Xylene	108-38-3	9,12	71,95	-	-	9,14	80,97
p-Xylene	106-42-3	11,01	84,41	10,21	91,63	10,95	97,32
o-Xylene	95-47-6	12,44	69,69	12,28	85,69	12,57	76,18
R_T – retention time, P – probability of identification (NIST Standard Reference Database).							

Chromatogram of sample pyrolysed at a temperature of 500 °C contained a small intensive peaks from aromatic hydrocarbons. A toluene peak was the highest. This is due to its construction and stability in temperature of 500 °C.

On chromatogram of sample pyrolysed at a temperature of 900 °C, a significant increase in relative intensity of peaks was observed. From peaks visible on chromatogram obtained at a temperature of 500 °C, the main peaks from benzene and ethylbenzene were the highest. Peak from m-xylene disappeared.

At a temperature of 1100 °C, an increase in intensity of benzene peak was observed within the range of retention times 1-1,5 min. An decrease in intensity of others peaks was observed in the range of retention times 3-13, which was caused by An increase in benzene peak area. These small peaks originated from degradation of the other aromatic hydrocarbon and their transformation into the structure of benzene.

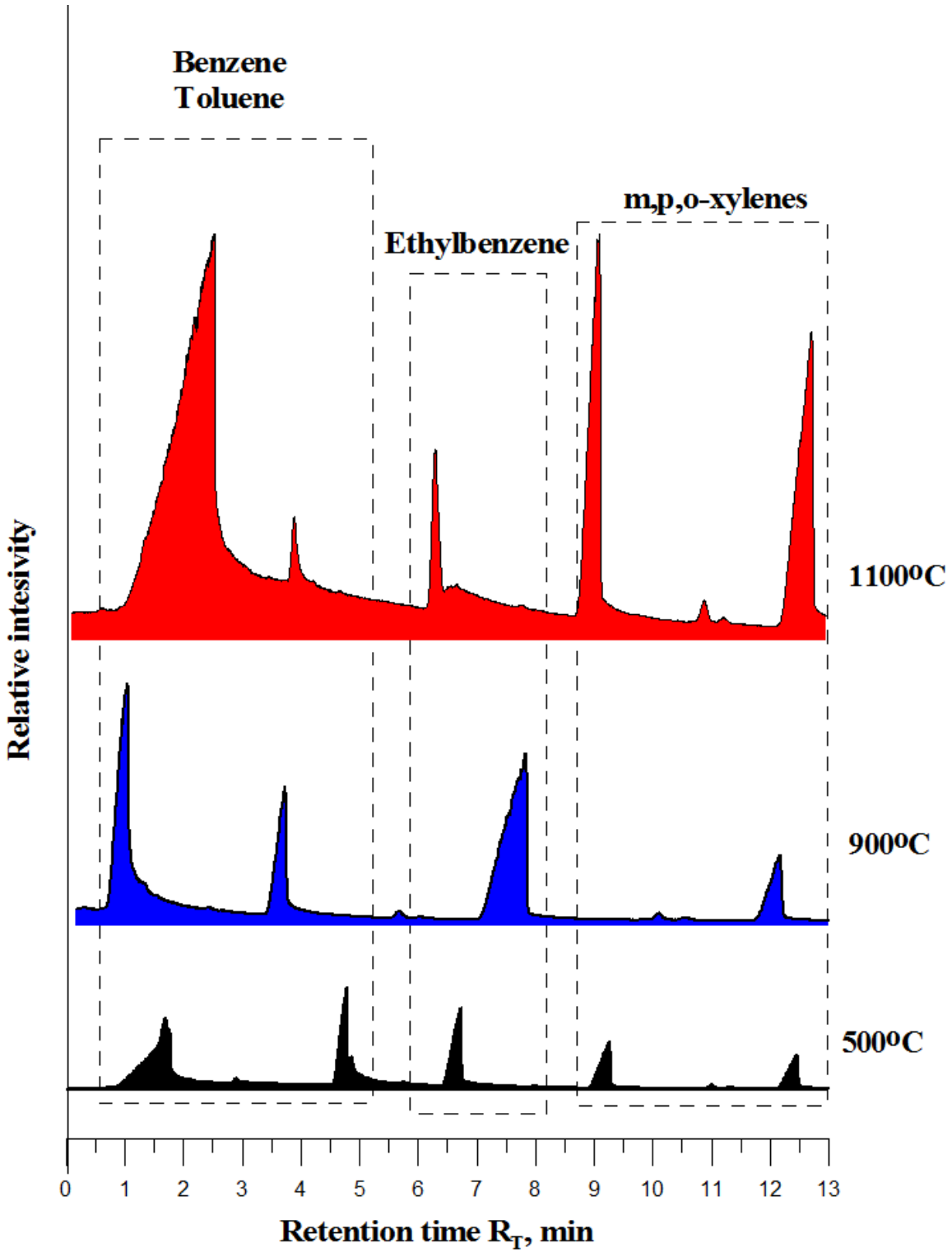

Figure 4. Chromatograms of tested materials.

3. CONCLUSIONS

A method of analysis by gas chromatography with application of a pyrolyser and coupled with a GC/MS set was developed. Application of a mass spectrometer as a detector has some advantages. The most important is that the significant increase in the amount of information delivered during analysis makes the process of interpretation of the obtained results easier (e.g. possibility of directly viewing the mass spectrum of a given peak), even when the retention time for a particular compound is little changed (Lachowicz, 2012). The possibility of observing the mass spectrum is also very useful in the case of peaks of important compounds having similar retention times thus allowing their correct identification.

The use Py-GC/MS analysis has enabled the identification of compounds from the group BTEX. This method can be successfully applied to assess the environmental performance of foundry binders. The harmfulness of binder is determined mainly by the emission of gases during foundry process like: casting or cooling. The disadvantage of this method is the ability to perform only a qualitative analysis of tested materials. In the case of an investigational binder, most of generated substances are not neutral to the human body, and a lot of them are hazardous (benzene, toluene). In people exposed to these compounds may increase the morbidity of lung cancer.

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