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Determination of Content of Phenol in Foundry Resins by Pyrolysis Gas Chromatography-Mass Spectrometry Method

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Abstract

In the foundry industry, many harmful compounds can be found, which as a result of gradual but long-term exposure to employees bring negative results. One of such compounds is phenol (aromatic organic compound), which its vapours are corrosive to the eyes, the skin, and the respiratory tract. Exposition to this compound also may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma. Phenol is a component of many foundry resins, especially used in shell moulds in the form of resin-coated sands. In order to identify it, the pyrolysis gas chromatography-mass spectrometry method (Py-GC/MS) was used. The tests were carried out in conditions close to real (shell mould process – temperature 300°C). During the measurement, attention was focused on the appropriate selection of chromatographic analysis conditions in order to best separate the compounds, as it is difficult to separate the phenol and its derivatives. The identification of compounds was based on own standards.

Keywords: Environment Protection, Innovative Foundry Technologies and Materials, Gas Chromatography, Pyrolysis, Phenol.

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1. Introduction

Foundry engineering belongs to an industrial branch of an increased professional risk. During the production process workers are exposed to dangerous and harmful agents, among which the emission of hazardous substances is essential [1, 2].

One of the sources of hazardous substances are moulding sands containing resins, which at high temperatures undergo thermal decompositions. Depending on the kind of the applied binder, under such conditions, the following substances can be formed and emitted to the environment: phenol, formaldehyde, furfuryl alcohol, aromatic hydrocarbons from BTEX group (benzene, toluene, ethylbenzene, xylenes), PAHs (polycyclic aromatic hydrocarbons) etc. [3-5].

Phenolic resins are a group of the most versatile polymers. Although they came into existence at the very start of the age of polymers, they continued to be developed into more and more applications. Usually phenolic resins are divided into two different types, novolacs and resoles. Both have high temperature stability up to about 350°C, high water and chemical stability [3, 6]. The phenol is the one of main compounds of foundry resins used in the cold-box technology, but also for resin-coated sands used for forming hot core blocks and shell moulds.

Phenol is not classifiable as to its carcinogenicity to humans but its vapors are corrosive to the eyes, the skin, and the respiratory tract. Its corrosive effect on skin and mucous membranes is due to a protein-degenerating effect. The substance may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma [6-10].

2. Tested materials

The tested materials included resin-coated sands (based on phenolic resin) used in the production of foundry hot cores and shell moulds (called S1, S2 and S3). Table 1 presented short characteristic of materials.

In the process of production resin-coated sand, quartz sand is heated in a special heating apparatus to temperatures of 120 to 150°C. Hot sand is mixed up in a core sand mixer together with phenolic resin (for e.g. solid flake-shaped); the resin melts and covers the quartz grains. This process step is referred to as premixing (premixing time is between 40 and 60 seconds). Then, hexamethylenetetramine (hardening agent) solved in water and calcium stearate (for better mixing) are added. The mixing time of this second step is 60 to 120 seconds. The hardening process is decelerated by subsequently cooling the mould material to 70 to 80°C. After removing the still lumped mould material from the mixer, it is pulverized on a vibrating screen where a well pourable mould material is formed which is cooled down to approx. 40°C [1, 10-12].

Table 1.
Characteristic of the materials (% composition in relation to quartz sand)

Compounds	S1	S2	S3
Hexamethylenetetramine	0,600	0,260	0,490
Resin	5,070	3,050	4,730
Phenol	0,051	0,031	0,023
Salicylic acid	0,152	0,092	0,190
Bisphenol A	-	-	0,095
Calcium stearate	0,080	0,130	0,170

3. Research methodology

The aim of the research was to use the pyrolysis gas chromatography-mass spectrometry method (Py-GC/MS) to assess the phenol emission from resin-coated sands (based on phenolic resin) used in the production of foundry hot cores and shell moulds. Gas chromatography is one of the useful techniques, which permits to determine the percentage composition of mixtures of chemical compounds. The good point of this method is, among others, its high sensitivity due to which very small samples of the analyzed substances can be used (approximately 1µl or 1 mg) [13, 14]. Identification of phenol was carried out by means of the pyrolysis gas chromatography-mass spectrometry method. The process parameters are shown in Figure 1.

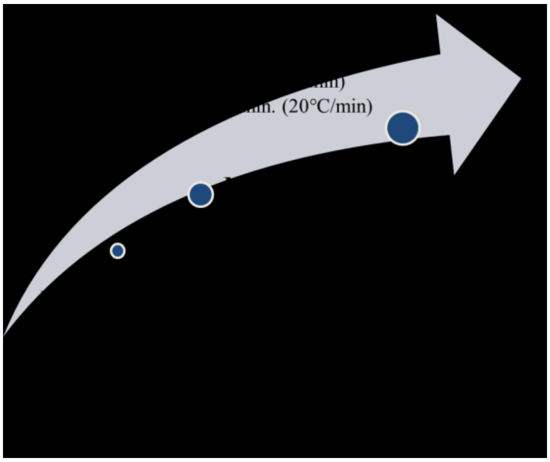

Fig. 1. The parameters of the Py-GC/MS process

4. Results and discussion

Figures 2-5 present the results of research in the form of chromatograms for the tested materials. The chromatograms contain the main signals come from carbon dioxide and phenol, and in the case of samples S3 – small content of benzene was identified. The area for a retention time of more than 30 minutes contains signals related to the column coating (stationary phase: 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane) and was not analyzed. The tested materials contain in their chemical composition mainly: phenol, salicylic acid, hexamethylene-triamine and calcium stearate (base for all) and in the case of sample S3 additionally bisphenol A (increased carbon dioxide emission in the chromatographic spectrum – Fig. 4).

The phenol emission was the highest for sample S2 and S3, the smallest for sample S1 (Table 2). Probably this is due to the higher proportion of resin in sample S3 or too little hardener (no total polymerization of the binder). However, phenol emission values are small and do not exceed 10% in relation to the whole sample volume (Threshold limit value TLV = 7,8 mg/m^3).

Table 2.
Emission of phenol in tested samples

Sample	Phenol (free) emission, µg/mg	Relation to the volume of the whole sample	
		%	mg
S1	34,86	3,49	0,523
S2	83,63	8,36	1,254
S3	94,22	9,42	1,413

In the initial phase of chromatographic analysis (retention time between 2-10 minutes) there are numerous small signals from the emission of simple hydrocarbons (such as cyclopenta-diene), whose detection is at the border of the noise coming from the baseline. For retention time between 19 and 22 minutes there is a characteristic, big signal from phenol emission and smaller from its derivatives (Fig. 5).

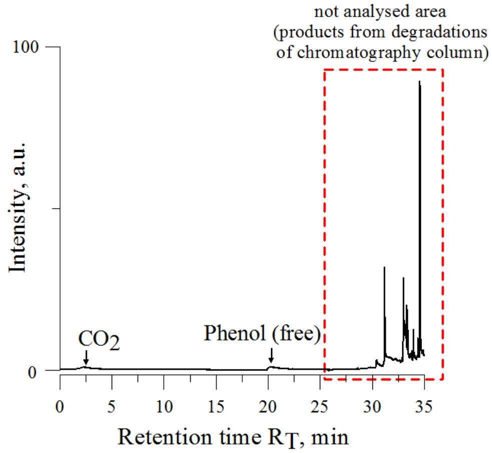

Fig. 2. Chromatogram of sample S1

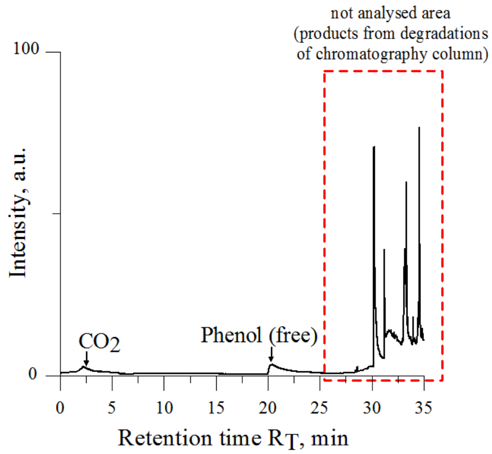

Fig. 3. Chromatogram of sample S2

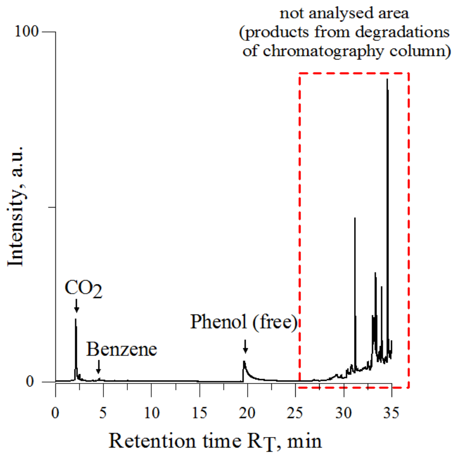

Fig. 4. Chromatogram of sample S3

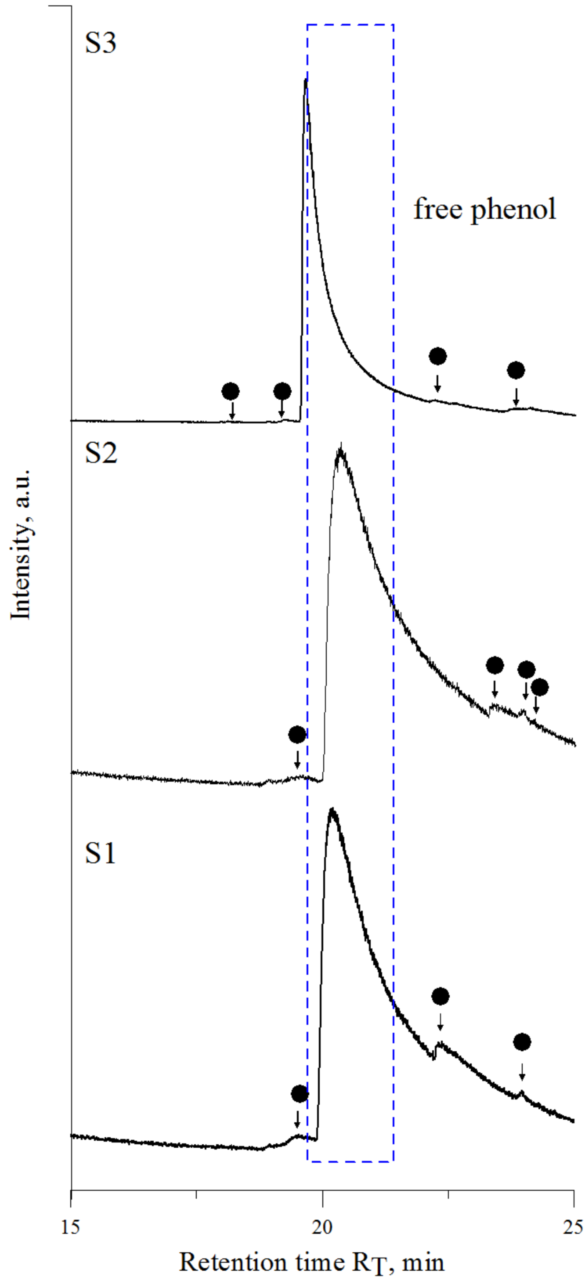

Fig. 5. Chromatograms with marked signal of emission of phenol and its derivatives (black dots)

Among the phenol derivatives, the largest group is cresols, 2,6-dimethylphenol, 2,3,6-trimethylphenol (black dots on Fig. 5). At 300 degrees, the identification of phenol is problematic. The wide area under the signal assigned for this compound also contains some of its derivatives. Probably, when changing the chromatographic column with a longer length, the separation would be more pronounced.

5. Conclusions

The research shows that the identification of phenol by pyrolysis gas chromatography-mass spectrometry method (Py-GC/MS) is possible and reliable, especially based on the internal standards of the compounds. In the samples of tested resin-coated sands, the phenol emission does not exceed the environmental standards, however, it is the highest for samples S2 and S3. After taking into account the user's properties, the chemical composition needs to be adjusted in order to achieve the lowest possible phenol emission. the process of separating the compounds from the gas mixture is difficult but possible.

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