

DETERMINATION OF THE PHENOL COMPOUNDS IN CONCRETE USING GC-MS

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Abstract

Organic contaminants from building materials negatively affected people's health. This study presents the validation of the analytical method, developed for the simultaneous identification and quantification of 9 phenolic compounds: phenol, 2-chloro phenol, 2,4-dimethyl phenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 4-chloro-3-methyl phenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrahydrophenol, pentachlorophenol in solid-solid concrete by gas chromatographic method with mass spectrometric detection (GC-MS). By comparing the MS spectra of the test compounds with MS spectra of analytical standards, reliable identification was achieved. The method can be applied in a given range (from 0.01 to 7.5 mg/kg) with the appropriate parameters precision, accuracy, repeatability and linearity. The developed method could be used for the quality control testing of phenols in concrete during the construction of new buildings and the old residences.

Introduction

Phenol and phenol derivatives represent a very important group of pollutants due to their toxicity and carcinogenicity, as well as possibilities accumulation in the environment [1]. Nowadays, considerable attention has been devoted to the problem of phenols' emission into the indoor area of buildings. The quality of the indoor air depends largely on outdoor air quality, but it can be affected by a number of other factors such as emissions from building materials (concrete, coatings, paint, lacquer) [2]. To date, due to the various sources of indoor air pollutants, there is no EU legislation relating to indoor air quality.

Although, EU-LCIWORKING GROUP has made the proposal of LCI (Lowest concentrations of interest) for dangerous substances emitted from building materials into indoor air [3]. Concrete is a composite building material made up of water, aggregate (rock, crushed stone, sand, or gravel), a binder or paste such as cement and may contain additives [4]. As such, it presents a complex and challenging matrix for phenols analysis. The aim of the presented study is to develop and validate GC-MS method for determination of 9 phenol compounds from samples of solid-solid concrete that were prepared by solid-liquid extraction. The main emphasis is on assessing the parameters of validation such as selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy and precision. This method could be used for control testing of phenols in buildings material during construction, porous concrete pavements or any other construction which contain concrete. Also, the validated method could be used for evaluation of phenol removal process.

Experimental

The following chemicals were used: Helium 5.0 (Messer Tehnogas), Phenol calibration mix 15, Phenol-Mix 15 2000 mg/L in methanol (Dr. Ehrenstorfer GmbH), Cyclohexane, HPLC grade (Fisher chemical), Methanol, CH₃OH (Macron Fine Chemicals), Potassium carbonate, K₂CO₃, pro analysis (Lach:ner), Hydrochloric acid, 36.5-38.0% (Sigma-Aldrich), Acetic acid anhydride, (CH₃•CO)₂O, (Mercks reagenzien), Sodium hydroxide, NaOH, 99% (Hemos), Sodium sulphate anhydrous, Na₂SO₄, 99% (Centrohem).

Chromatographic analyses were carried out on the Gas chromatograph with mass detector - Agilent Technologies 7890B GC System, Agilent Technologies 5977MSD.

Sampling of the concrete walls was carried in the dimensions 10×10 cm, with a drill, with diamond plate, to the depth of 2 cm. The concrete was then collected in a hermetically sealed container and transported to the laboratory. Furthermore, the sample was homogenized to the particle size <1 μm by the hydraulic press without heating.

The basic standard solution of phenolic compounds (phenol, 2-chloro phenol, 2,4-dimethyl phenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 4-chloro-3-methyl phenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrahydrophenol, pentachlorophenol) in methanol in concentration of 2000 mg/L was supplied from the manufacturer in liquid form. Working solution of 50 μg/ml was prepared by diluting the basic solution of phenol in methanol. In 10 g of dry sample (dry matter determined according to SRPS EN 14346: 2012), working standard solution of phenol was added at concentrations of 0.1 mg/L, 0.5 mg/L and 1.0 mg/L (7.50, 3.75 and 1.88 mg/kg). In a measured 10 g sample - dry mass (dry matter determined according to SRPS EN 14346: 2012), an intermediate standard solution of phenol was added at concentrations of 0.1 mg/L, 0.5 mg/L and 1.0 mg/L (7.50, 3.75 and 1.88 mg/kg). The sample preparation was performed by a modified solid-liquid extraction as described in literature [25]. 75 ml of methanol was added to each spike and pH <3 was adjusted by adding concentrated hydrochloric acid (for a concrete 1 ml of HCl, for a country 0.5 ml of HCl). Extraction was performed by strong shaving for 10 minutes on an ultrasonic bath, then 30 minutes on a mechanical shaker (200-300 rpm). After the particles settled, the supernatant was filtered. An aliquot of 10 ml was transferred to a separation funnel of 100 ml and 50 ml of aqueous potassium carbonate solution (0.1M) was added. Then, 2 ml of sodium hydroxide (0.5M) and 1 ml of acetic anhydride were added to the extract. Extract was trembled for 2 minutes with the release of carbon dioxide that occurs in the separating funnel, left 10 minutes to stand with occasional shaving. After the timeout, 10 ml of cyclohexane was added. It was intensely shaken and the two phases were separated. The cyclohexane phase (upper phase) was transferred to a head space of 20 ml in which 2 g of anhydrous sodium sulfate was previously dosed. The extract was stored in a refrigerator at 4 [deg.] C. and analyzed before 48 h. 1 ml of GC-MS extract was taken. Blank sample was prepared in the same way as a real sample. Identification of compounds from the standard was performed by comparing the characteristic mass spectrum of the compound from the library with the characteristic MS spectrum of the individual phenol in the standard solution.

Results and discussion

This paper presents a validated and developed a modern, precise and accurate, analytical GC-MS method for identification and quantification of phenol compounds in concrete. By comparing the MS spectra of the test compounds with MS spectra of analytical standards, reliable identification was achieved. The selectivity of the method was tested by calculation of the resolution successive peak at chromatogram of the spiked sample of concrete (Figure 1.).

A good resolution of the analyzed peaks was achieved using the GC-MS technique. The linearity of the method was tested by regression analysis. Limits of detection (LOD) and quantification (LOQ) were determined statistically using regression analysis functions obtained for linearity. Recovery test was used to check the accuracy of the method. The precision of the presented analytical method is expressed as the relative standard deviation (RSD (%)) of measurements under repeatability conditions when an analysis is performed by a single analyst using the same equipment over a short timescale. The main validation parameters of method are presented in Table 1. MS detector shows a linear response in a concentration range of 0.05 to 1 mg/L (0,01 to 7,5 mg/kg) with correlation coefficients $R \geq 0.98$. The accuracy of method is proved by the relative standard deviation below 5.0%. Reproducibility of the method is, indicated by a relative standard deviation of below 10.0%.

Table 1. Summary of the method validation data

Phenol	Rt± s (min.)	Regression equation	R	LOD (mg/kg)	LOQ (mg/kg)	Repeatability of the method RSD	Precision of the method RSD	Recovery %
phenol	2,959± 0,05	y=493433,108*x	0,992	0,0033	0,01	0,04	0,08	78,8
2-chloro phenol	3,703 ± 0,05	y=416100,92*x-9887,796	0,999	0,004	0,01	0,037	0,081	87,02
2,4-dimethyl phenol	3,926 ± 0,05	y=500446,669*x-10495,35	0,997	0,025	0,08	0,0303	0,0635	33,72
2,4-dichlorophenol	4,647 ± 0,05	y=394625,602*x-10262,29	0,998	0,025	0,08	0,05	0,07	86,61
2,6-dichlorophenol	4,510 ± 0,05	y=343841,22*x-6017,669	0,999	0,003	0,01	0,048	0,095	91,03
4-chloro-3-methyl phenol	4,561 ± 0,05	y=201366,61*x-4856,93	0,998	0,003	0,01	0,035	0,068	83,88
2,4,6-trichlorophenol	5,402 ± 0,05	y=246943,03*x-6070,09	0,997	0,003	0,01	0,041	0,0631	88,4
2,3,4,6-tetrahydrophenol	7,153 ± 0,05	y=109197,001*x-4218,06	0,992	0,025	0,08	0,027	0,0907	89,03
Pentachlorophenol	8,664 ± 0,05	y=82373,24*x-5042,42	0,985	0,03	0,1	0,049	0,068	85,13

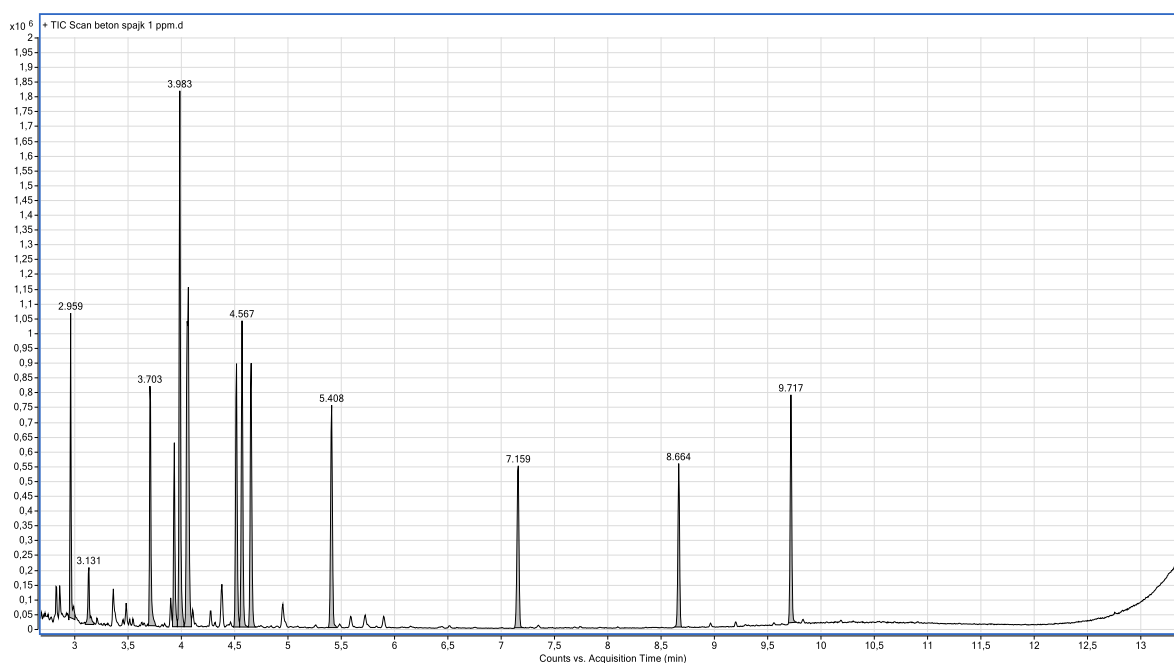


Figure 1. The chromatogram of concrete spiked with phenols solution (7,5 mg/kg)

Conclusion

The method for the simultaneous identification and quantification of the nine phenols compounds in solid–solid concrete by gas chromatographic method with mass spectrometric detection analytical technique was developed and validated in presented study. Based on precision, accuracy, repeatability and linearity, it can be concluded that the measuring range of developed method ranged from 0.01 to 7.5 mg/kg. Good resolution of the analyzed peaks was achieved using the GC-MS technique. The developed method will be used for the control testing of phenols in concrete in new buildings and old buildings associated with a sick-building syndrome.

Acknowledgements

This study was financially supported by the "Serbian Ministry of Education, Science and Technological Development" (Grants No. 172045 and 37021).

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