

## CHROMATOGRAPHIC TECHNIQUES FOR THE DETERMINATION OF FREE PHENOL IN FOUNDRY RESINS

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### ABSTRACT

Phenol is a toxic compound present in a wide variety of foundry resins. Its quantification is important for the characterization of the resins as well as for the evaluation of free contaminants present in foundry wastes. Two chromatographic methods, liquid chromatography with ultraviolet detection (LC-UV) and gas chromatography with flame ionization detection (GC-FID), for the analysis of free phenol in several foundry resins, after a simple extraction procedure (30 min), were developed. Both chromatographic methods were suitable for the determination of phenol in the studied furanic and phenolic resins, showing good selectivity, accuracy (recovery 99–100%; relative deviations <5%), and precision (coefficients of variation <6%). The used ASTM reference method was only found to be useful in the analysis of phenolic resins, while the LC and GC methods were applicable for all the studied resins. The developed methods reduce the time of analysis from 3.5 hours to about 30 min and can readily be used in routine quality control laboratories.

Keywords: Foundry resin; Gas chromatography; Liquid chromatography; Phenol

### INTRODUCTION

Phenolic compounds are considered micropollutants and are carcinogenic agents and endocrine disruptors (Kim and Kim 2000), which are mainly introduced in the environment by industrial activities. The presence of phenol in tap water and water wells can seriously affect human health. Phenol and its mono-substituted analogues are easily transferred to and transported in the aquatic environment. Because of these features, many phenolic compounds are included on the EU and USEPA's lists of priority pollutants.

Therefore, the monitoring of phenol is important in several environmental, clinical, toxicological, and industrial areas. Phenol is present in a wide variety of foundry resins. Its quantification is important for the characterization of the resins as well as for the evaluation of free contaminants present in foundry wastes.

A large number of studies have been published regarding the analysis of phenol by many analytical methodologies in a wide variety of matrixes, especially environmental samples. The most widely used techniques for the analysis of phenolic compounds are gas and liquid chromatographic techniques (Robards 2003; Gentili, Marchese, and Perret 2008; Hajek et al. 2008; Huang, Qiu, and Yuan 2008; Kovacs et al. 2008; Shi et al. 2008; Vichi et al. 2008; Wu, Hu, and Hou 2008; Xu et al. 2008; Zafra-Gomez et al. 2008).

Regarding the analysis of free phenol in resins, as far as it is known, only a few works are described in the literature, the latest being published over 35 years ago. The analytical methods used were infrared spectrometry (Smith, Rugg, and Bowman 1952), titration after steam distillation and colorimetric analysis (Haslam, Whettem, and Newlands 1953), gas chromatography (Stevens and Percival 1964) and gel permeation chromatography (Tsuge, Miyabaya, and Tanaka 1973). These studies were performed using acidic phenolic resins and do not include the most widely used resins today: furanic and alkaline phenolic resins. The majority of the proposed methods are time-consuming and/or use harmful reagents. Besides these studies, the American Society for Testing and Materials (ASTM) issued a standard method of test for the analysis of free phenol in synthetic phenolic resins (ASTM D1312-93). This method includes a time-consuming steam distillation followed by a volumetric analysis.

The most widely used resins in the Portuguese foundry industry are furanic and phenolic resins. Furanic resins are obtained by the reaction of furfuryl alcohol and formaldehyde at an acidic pH. In these resins, phenol is used as an additive to enhance its molding and processing characteristics. Like this, free phenol concentration in these resins is expected to be low. Phenolic resins are obtained by condensation polymerization of phenol and formaldehyde in either acidic or alkaline media. Therefore, the free phenol content of the resins is expected to be relatively high. Because of recent EU legislation, which establishes a maximum amount of free phenol in resins, the analysis of phenol content in phenolic resins became even more important. The analytical methods used for this purpose were liquid chromatography with ultraviolet detection (LC-UV) and gas chromatography with flame ionization detection (GC-FID). These methods were chosen because they are available in the majority of laboratories for routine analysis, unlike the more sophisticated and expensive chromatographic methods coupled to mass spectrometric detectors (MS), namely GC-MS and LC-MS. A simple extraction method to reduce the analysis time was also optimized. Our objective was to develop two chromatographic applications for the analysis of free phenol in foundry resins. The advantages of these applications are (1) applicability to all (including furanic) resins; (2) reduced analysis time; (3) adequate LOD values regarding the established limits by law; and (4) the use of low-cost chromatographic equipment.

## EXPERIMENTAL

### Apparatus

Liquid chromatographic analyses were performed using a Sykam 1210 LC system, with a 20-mL injection valve, connected to a Sykam 3200 UV=Vis detector and a PC running PRIME 2.2.6 integration software. The LC separations were carried out with an ET Nucleosil C<sub>18</sub> column (250 mm × 4.6 mm; 5 mm particle size) from Macherey-Nagel followed by UV-detection at 273 nm. Isocratic elution using a mixture of acetonitrile and water (40:60; v=v) was performed at a flow rate of

1.3 mL min<sup>-1</sup>. Both solvents were previously filtered through 0.45-mm PTFE filters (Tracer) and degassed with helium. Before injection, the solutions were filtered through 0.22-mm polypropylene filters (Tracer). All analyses were carried out at room temperature.

A Chrompack CP 9000 gas chromatograph equipped with an FID detector and controlled by a PC running Maestro 2.4 software (Chrompack International) was used for the GC analyses. Separations were achieved with a Chrompack CP-Wax 52CB column (25 m × 0.53 mm), using nitrogen as the carrier gas (flow rate: 7 mL min<sup>-1</sup>); nitrogen was also used as make-up gas. The separations were performed at 150°C during 3.5 min after which the temperature was risen to 200°C at 20°C min<sup>-1</sup>. Injection and detector temperatures were 230°C. Sample volumes of 1 mL were directly injected.

In the reference method (ASTM 1312-93) a custom steam distillation set-up and an automatic buret (Metrohm 715 Dosimat) were used.

### Reagents and Solutions

Deionized water, which was further purified by an E-pure 4 system (Barnstead), was used throughout the study (conductivity <0.06 mS cm<sup>-1</sup>). All chemicals were analytical reagent and purchased from Merck, including the phenol standard (99.5%) and acetonitrile (Lichrosolv).

The phenol stock solution (1000 mg L<sup>-1</sup>) was prepared by dissolution of the standard in water and was afterwards titrated using a reference method (Greenberg 1992) to determine its concentration. When stored in absence of light this stock solution was stable for several months. The used standard solutions (5–160 mg L<sup>-1</sup>) for the chromatographic determinations were prepared daily by dilution of the stock solution with methanol (GC) or with a mixture of acetonitrile and water (60:40; v=v) (LC).

### Samples

Different kinds of resins were provided by different suppliers: three furanic resins (F1, F2, and F3), two acidic phenolic resins (PAC1 and PAC2) and one alkaline phenolic resin (PAL1). An adequate amount of the resin sample (0.12–2.5 g) was mixed with 250.0 mL of water and the mixture was shaken for 30 min at room temperature to assure the complete extraction of phenol. Afterwards, this solution was filtered and a 20-mL aliquot was injected into the liquid chromatograph. For GC analysis a suitable amount (between 50 and 1000 mL) of the sample solution

was diluted to 10.00mL with methanol and injected into the gas chromatograph ( $V_{inj} \frac{1}{4} 1 \text{ mL}$ ).

The accuracy of the results of the analysis in the phenolic resins was validated by comparing the results with the ASTM reference method. In this method free phenol was extracted from the resins by steam distillation, reacted with an excess of bromine, and the excess back-titrated with a standard sodium thiosulfate solution. The total analysis time using this procedure was about 3.5 hours.

However, it is important to note that the reference method cannot be applied for the analysis of the furanic resins because of the interference of furfuryl alcohol present in these samples. Therefore, for these samples recovery assays were used to evaluate the accuracy of the results; an amount (50–1000mL) of the extracted sample solution was spiked with 100 mL of a standard phenol solution ( $160 \text{ mg L}^{-1}$ ) and diluted to 10.00 mL with the appropriate solvent.

## RESULTS AND DISCUSSION

In order to determine the detection wavelength for the LC analysis the absorption spectrum (UV) of a standard phenol solution was recorded, obtaining maximum absorption peaks at 219 and 273 nm. The latter wavelength was considered adequate for the analysis of phenol in the resins and was used in all subsequent LC analyses. The linear range between phenol concentration and analytical signal was established by analyzing several standard solutions. The characteristics of the linear calibration curve and the limit of detection (LOD) calculated using this curve (Miller and Miller 2000; ISO 8466-1 1990) are indicated in Table 1. Accordingly, and after the optimization of the GC conditions, the linear range and the LOD were also established for this method (Table 1).

When compared, the LC method provides a larger linear range than the GC method and no significant differences were found in the achieved LODs.

The possible interference of other compounds commonly present in resins, especially furfuryl alcohol and formaldehyde, was studied by analyzing mixtures of phenol with these compounds. In the LC analysis, formaldehyde ( $100 \text{ mg L}^{-1}$ ) does not interfere because it does not absorb radiation of the used wavelength

Table 1. Characteristics of the calibration curves and limits of detection of the analysis of phenol by LC and GC

	LC	GC
Concentration range (mg=L)	10–160	5–43
Correlation coefficient	0.9996	0.9998
Slope	291	2700
Intercept	–656	390
Residual standard deviation ( $S_{Y=X}$ )	159	1087
Standard deviation of the method ( $S_{X0}$ )	0.54	0.40
Coefficient of variation of the method ( $V_{X0}$ )	1.7%	1.9%
LOD (mg=L)	1.64	1.10

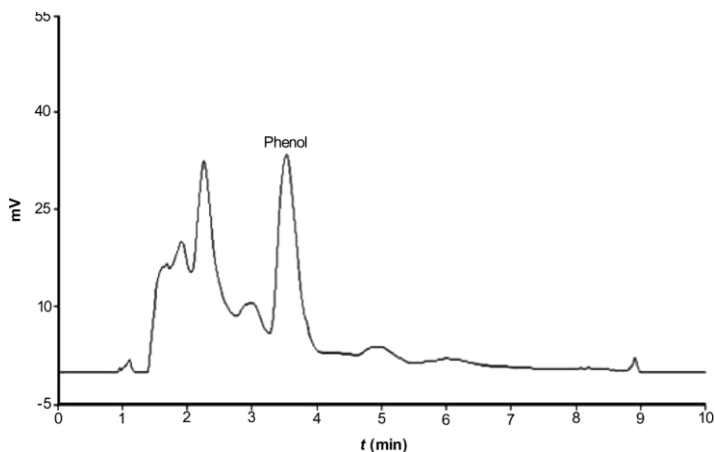


Figure 1. Chromatogram (LC) of the analysis of PAC2, an acidic phenolic resin.

(273nm) and does not alter the chromatographic peak areas. Formaldehyde also does not interfere in the GC analysis due to the low sensitivity of the FID detector towards this compound. Regarding furfuryl alcohol, which is present in large quantities in the furanic resins (Oliva-Teles, Delerue-Matos, and Alvim-Ferraz 2005), this compound does not interfere in both the LC and GC analysis. A good separation of the GC peaks of phenol and furfuryl alcohol was observed. Moreover, furfuryl alcohol has a maximum absorption at 220nm and does not absorb radiation of the used wavelength.

Chromatograms of the analysis of the most complex resins are shown in Figure 1 (LC) and Figure 2 (GC). The resolution between the LC peaks for phenol and an unidentified matrix component was 0.95 for this resin. For the other resins the resolutions were higher (complete separations were obtained), making the

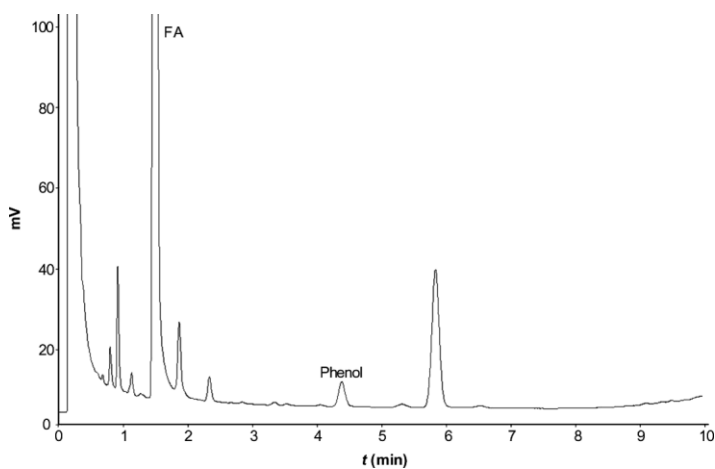


Figure 2. Chromatogram (GC) of the analysis of F3, a furanic resin.

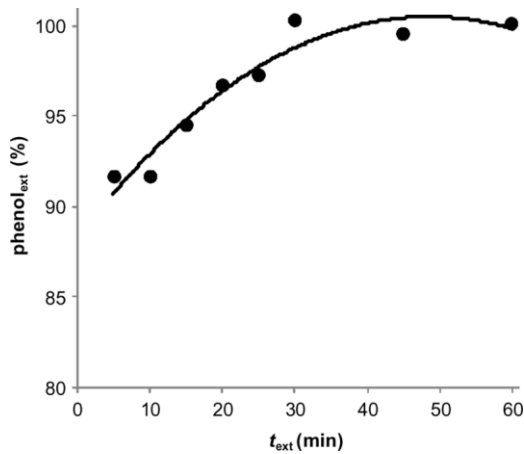


Figure 3. Optimization of the extraction time of free phenol (PAC1).

separations adequate in all cases. Good resolutions of the analyte peaks were observed for the GC analysis. This indicates that the methods provided an adequate selectivity for the proposed analysis. Although the ASTM reference method is issued for phenolic resins, it was also tested for the furanic resins. It was found that furfuryl alcohol had a significant interference in this method because it reacts with bromine used in the titration. Hence, this method was only applied to the phenolic resins.

To optimize the extraction time an acidic phenolic resin (PAC1) was selected and LC was used for the analysis. Figure 3 shows that an extraction time of 30 min was adequate, reason why it was used in all subsequent experiments. This extraction time was found to be adequate for all the other resins.

Table 2 presents the results of the analysis of phenol (expressed as mass percentage values) in the selected resins by the developed methods (LC and GC) and the ASTM reference method. Coefficients of variation (CV) based on 9 determinations are also included, the results obtained allowed the conclusion that all the used methods presented a good precision (CV  $\pm 6\%$ ), the LC method being the most precise. The obtained relative deviations ( $\pm 12\%$ ) indicated that the results of all

Table 2. Mean values of free phenol content in the selected foundry resins for the LC, GC, and ASTM methods and relative deviations between the results of the used methods

Resin	Phenol content (% w=w) <sup>a</sup>			Relative deviation (%)		
	LC	GC	ASTM	GC - LC	Ref - LC	Ref - GC
F1	1.07 ( $\pm 2\%$ )	0.95 ( $\pm 4\%$ )	na	-12	-	-
F2	0.79 ( $\pm 5\%$ )	0.84 ( $\pm 6\%$ )	na	6	-	-
F3	0.68 ( $\pm 2\%$ )	0.621 ( $\pm 1\%$ )	na	-9	-	-
PAC1	11.1 ( $\pm 3\%$ )	11.0 ( $\pm 0.8\%$ )	11.3 ( $\pm 0.3\%$ )	-1	2	3
PAC2	10.8 ( $\pm 0.4\%$ )	10.7 ( $\pm 4\%$ )	10.7 ( $\pm 5\%$ )	-0.8	-0.5	0.4
PAL1	0.448 ( $\pm 0.2\%$ )	0.45 ( $\pm 3\%$ )	0.430 ( $\pm 1\%$ )	0.4	-4	-5

<sup>a</sup>na: not applicable; coefficients of variation in parenthesis ( $n=49$ ).

methods are in agreement. Based on the comparison of the developed methods with the reference method, it was concluded that both the LC and the GC methods provide accurate results.

The results obtained in the recovery assays for the furanic resins were 99% (CV:::±3%) for LC and 100% (CV:::±7%) for GC. This indicates that both methods provide accurate and precise results for these resins.

## CONCLUSIONS

Both chromatographic methods (LC and GC) can be used for the quantification of free phenol in furanic and phenolic foundry resins, which is an advantage when compared with the reference method, which only can be used for phenolic resins. Although the foundry resins are complex, a simple extraction procedure, using water as solvent, can be used. Like this, the analysis can be performed in about 30 min, which dramatically reduces the 3.5-hour procedure of the reference method. Both methods provide accurate and precise results without interference from other compounds present in the studied resins. Regarding the previously published studies on the same subject, the main advantage is the use of more widely available equipment, allowing the implementation of the methods in laboratories for routine analysis.

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