Determination of free furfuryl alcohol in foundry resins by chromatographic techniques

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Abstract

Two chromatographic methods, gas chromatography with flow ionization detection (GC–FID) and liquid chromatography with ultraviolet detection (LC–UV), were used to determine furfuryl alcohol in several kinds of foundry resins, after application of an optimised extraction procedure. The GC method developed gave feasibility that did not depend on resin kind. Analysis by LC was suitable just for furanic resins. The presence of interference in the phenolic resins did not allow an appropriate quantification by LC. Both methods gave accurate and precise results. Recoveries were >94%; relative standard deviations were ≤7 and ≤0.3%, respectively for GC and LC methods. Good relative deviations between the two methods were found (≤3%).

Keywords: Foundry resins; Furfuryl alcohol; LC; GC

1. Introduction

Furfuryl alcohol (FA) is a very toxic component; maybe fatal if inhaled, and irritating to eyes, skin and respiratory tract; FA is listed as carcinogen by National Institute for Occupational Safety and Health (NIOSH) [1,2]. It is a liquid propellant, viscosity reducer, antioxidant and flavour ingredient. Furfuryl alcohol has useful range of applications like pharmaceutical, fungicide, insecticide and solvent fields. It is used as precursor to graphitic composition and adhesives and to produce tetrahydrofurfuryl alcohol, abrasive wheels or furanic resins [1,3], being employed as wetting agent and solvent for resins, for cellulose ethers and esters, for ester gum and for textile printing [1]. Particularly, in foundries, FA is one of the compounds present in the wide variety of organic bind resins, as a resin solvent but also as a binder of the foundry sands, used to produce cores and moulds [4]. Free FA quantification is important to the chemical characterisation of the resin itself and for the evaluation of free contaminants present on wastes generated by the foundry industry; according to FA toxicity, these environmental aspects are particularly important.

FA was controlled by ultraviolet (UV) spectrophotometric method, after a micro-distillation using water vapour for synthesis and characterisation of epoxidized phenolic novolacs modified by FA [5]. Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (H-NMR) and size exclusion chromatography contributed to the understanding of mechanisms of chromophore formation and cross-linking in acid-catalysed polycondensation of FA [3,6–8]. Amperometry was used to measure furanics in transformer oils [9]. Nevertheless, the chromatographic methods, including gas chromatography (GC) or liquid chromatography (LC), have been the most applied to quantify FA in different kinds of matrices.

Liquid chromatography with ultraviolet detection (LC/UV) methodology was used to measure the concentra-

tion of FA in a mixture of 11 phenols and 5 furans in 12 categories of distilled spirits [10], as degradation products in fruit juice and drinks [11] and in cellulose insulation paper [12]. LC/UV was also used to quantify the FA trapped in photochemical studies of a phototoxic muscle relaxant drug [13]. LC is the recommended method for furanic compounds in electrical insulating liquids [14].

GC procedure using flame ionization detector (FID) or mass spectrometry (MS) detection was also developed to determine FA in food and environmental samples: as volatile flavour component of rice cakes [15], of stored nonfat dry milk [16], of honey [17], of barrel-aged wines [18] and as a volatile constituents of used frying oil obtained from a local food processing plant [19]. FA was quantified by these methodologies in a list of 28 and 140 compounds, respectively. Determination of hydrophilic compounds, such as FA, was also performed by GC–MS in environmental water by solid-phase extraction with activated carbon fibber felt [20]. GC–FID is the method recommended for the analysis of FA in occupational environment [21].

Considering that GC–MS and LC–MS are not many times available for routine analysis, other common techniques should be implemented. The present paper describes two chromatographic methods (GC–FID and LC–UV) to determine free FA in several kinds of foundry resins. The complexity of their matrices and the presence of interferents were considered. The accuracy of the analytical procedure was assessed through recovery measurements. The resins selected are the most representatives for the Portuguese foundries: furanic, phenolic acid and phenolic alkaline.

2. Experimental

2.1. Apparatus

The GC system used was Chrompack CP 9000 equipped with a FID detector and connected to a computing integrator with a chromatographic data station (Maestro 2.4, Chrompack International). Separations were done in a CP-Wax 52CB column (25 m × 0.53 mm) from Chrompack, using nitrogen as carrier gas (flow rate: 7 ml min^{-1}); nitrogen was also used as make-up gas. Column temperature was programmed from 150 (3 min) to 200 °C (3 min) at 20 °C min^{-1}. Injection and detector temperatures were 230 °C. Direct injections (1 μl) were used.

The LC system used was a Sykam 1210 liquid chromatograph, equipped with a 3200 UV–vis detector and connected to a computing integrator with a chromatographic data station (PRIME 2.2.6). The system had an injection valve with a 20 μl loop. The chromatographic separations were done with ET Nucleosil C_{18} column (250 mm × 4.6 mm; 5 μm particle size) from Macherey-Nagel. To perform the isocratic elution at a flow rate of 1.3 ml min^{-1}, a mixture of acetonitrile and water (40:60, v/v) was used. Both solvents were previously filtered through 0.45 μm polytetrafluoroethylene (PTFE) filter (TR 200200, Tracer) and degassed with helium. Before injecting into the LC column, all solutions were passed through 0.22 μm polypropylene filter (TR 200112, Tracer). Analyses were carried out at room temperature.

2.2. Reagents and solutions

Water was deionised and further purified via an E-pure 4 system (Barnstead). Acetonitrile and methanol used were LC grade (Merck). The chromatography standard was 98% furfuryl alcohol (FA) employed from Riedel-de Häen; the other chemicals were analytical reagent grade from Merck.

Stock solution, 4430 mg l^{-1} FA, was prepared by dilution of 0.1 ml FA to 25 ml with methanol. This solution was stored in the dark, showing to be stable during several weeks. FA standard solutions (10–150 mg 1^{-1}) used in chromatographic determinations were diary prepared by dilution of the stock standard solution with methanol (GC analysis) or with a mixture of acetonitrile and water (60:40, v/v) (LC analysis).

2.3. Samples

Different kinds of resins were kindly provided by different suppliers: three furanic (FURAN1, FURAN2 and FURAN3), two phenolic acids (FENAC1 and FENAC2) and one phenolic alkaline (FENALC). An appropriate amount of the resin sample (0.5–2 g) was dissolved in 50.0 ml of methanol. The mixture was shaken during 30 min at room temperature, to assure that the extraction of FA was completely. Afterwards, a suitable amount (between 50.00 and 500.0 μl) of the sample solution was diluted to 10 ml with methanol (GC analysis) or with a solution of acetonitrile and water (60:40, v/v) (LC analysis).

To check results accuracy of all resins, recovery assays were carried out. An amount of a sample solution was spiked with 300 μl of FA stock solution and diluted to 10 ml, with the appropriate solvent. The interference of other compounds eventually present in resins, namely phenol and formaldehyde, was also considered. This study was carried out using 22 mg l^{-1} FA standard solution, spiked with an excess of the supposed interferent.

3. Results and discussion

Aqueous solutions of FA are unstable, but FA and the resins are soluble in alcohol. Therefore, the stock solution was prepared in methanol and in this solvent the solution was stable for several months. The chromatographic procedure was optimised and adapted to these particular matrices with very specific characteristics.

For GC determinations, methanol was the solvent chosen between others tested (acetonitrile, ethanol). Methanol was the solvent used in the sample extraction. Furthermore a good chromatographic separation between the solvent and the an-

alyte was achieved and no additional step was necessary. The column temperature was optimised considering the complexity of the matrices, being programmed from 150 (7 min) to 200 °C at 20 °C min^{-1}. The injection temperature chosen was 230 °C. The retention time obtained for FA was 1.8 min.

In LC procedure, the determinations of free FA were carried out at 220 nm near the FA absorption maximum. The mobile phase was a mixture of acetonitrile and water (40:60, v/v), since methanol is not transparent at this wavelength. The flow rate was 1.3 ml min^{-1}. The retention time obtained for FA was 2.3 min.

Standard calibrations were used for the quantification of free FA in resins by GC and LC methods. Using four standard solutions, with concentrations in the range of 10–150 mg l^{-1}, a linear response was obtained. For GC curve the correlation coefficient was 0.9998 and two-tailed Student's test calculated was 3.54, for a significant correlation lower than $p = 0.10$. For LC curve the correlation coefficient and the two-tailed Student's test were, respectively, 0.99991 and 7.86 (significant correlation lower than $p = 0.02$). The slope and intercept were, respectively, equal to 4816 and 114 for GC and 1192 and 64 for LC. It means that quantification can be performed on this range.

Using these conditions, the limit of detection were 173 μg l^{-1} for GC method, which is equivalent to 173 pg FA per injection (1 μl) and 5.2 mg l^{-1} for LC method, which is equivalent to 24.8 ng FA per injection (20 μl) [22]. The relative standard deviation for each solution was always less than 8 (GC) and 1% (LC).

Using LC technique the time of extraction of free FA from resins was studied based in FURAN3 analyses. Fig. 1 presents the mass percentage versus extraction time. According to the results, 30 min was selected.

Figs. 2 and 3 show typical chromatograms obtained by both methodologies for standard solutions and for two different kinds of resins (FURAN1 and FENAC1). The application of GC methodology on samples was well succeeded, leading to a good separation between the chromatographic peaks for the selected experimental conditions. Phenol and formaldehyde are compounds usually present in resin composition. Therefore, an interference study of these compounds on the developed method was performed, spiking the standard solution with an excess of the supposed interferents. Solutions with phenol had its chromatographic peak at 4.5 min. Since FID is not sensitive enough to detect formaldehyde, no additional peak was obtained for solutions with formaldehyde. So, these compounds did not interfere with free FA during GC analysis.

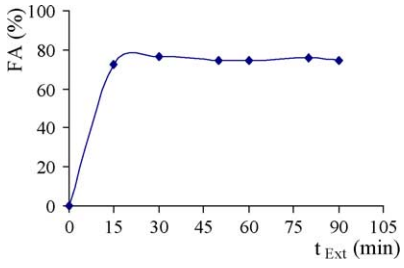

Fig. 1. Extraction time optimisation of free FA in FURAN3 (LC method).

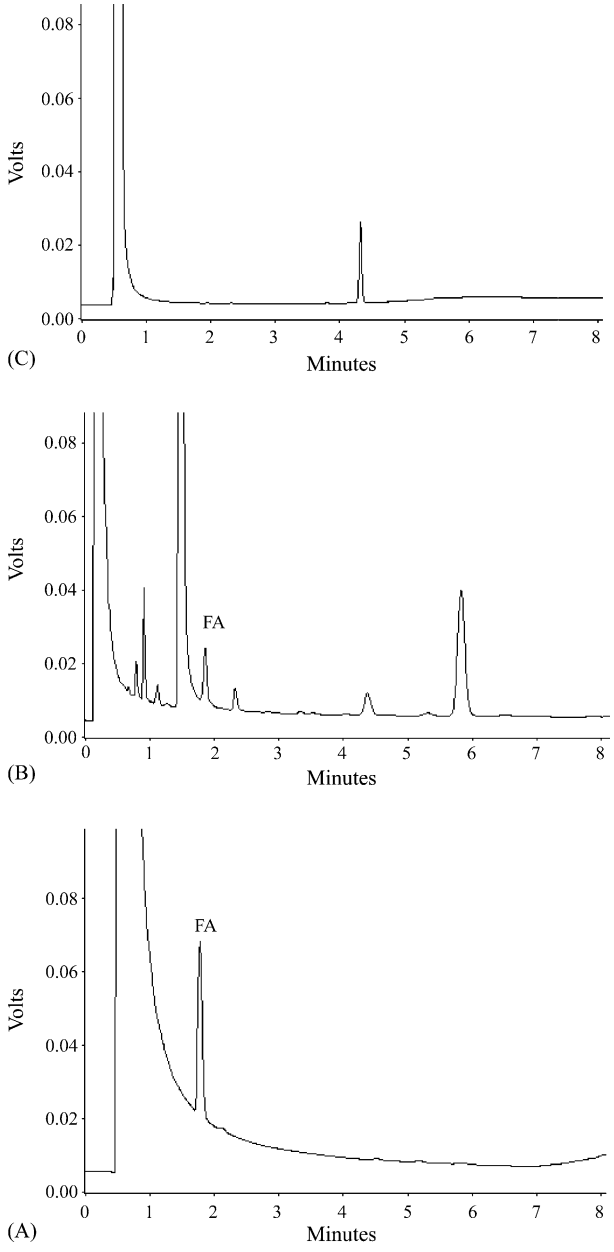

Fig. 2. Gas chromatograms obtained for 44 mg l^{-1} FA standard solution (A), for FURAN1 resin solution (B) and for FENAC1 resin solution (C).

The experimental conditions selected for LC analysis gave a good separation between the chromatographic peaks for the furanic resin (Fig. 3B). For phenolic resin, it was observed an apparent FA peak (Fig. 3C) not in accordance with the GC results (Fig. 2C) and with the value expected for that kind of resins. To solve this problem, those solutions were analysed using another wavelength such as 273 nm for the UV detection, the same used to detect phenol presents in samples. In this condition, FA did not absorb and the chromatograms of a standard mixture of these two compounds

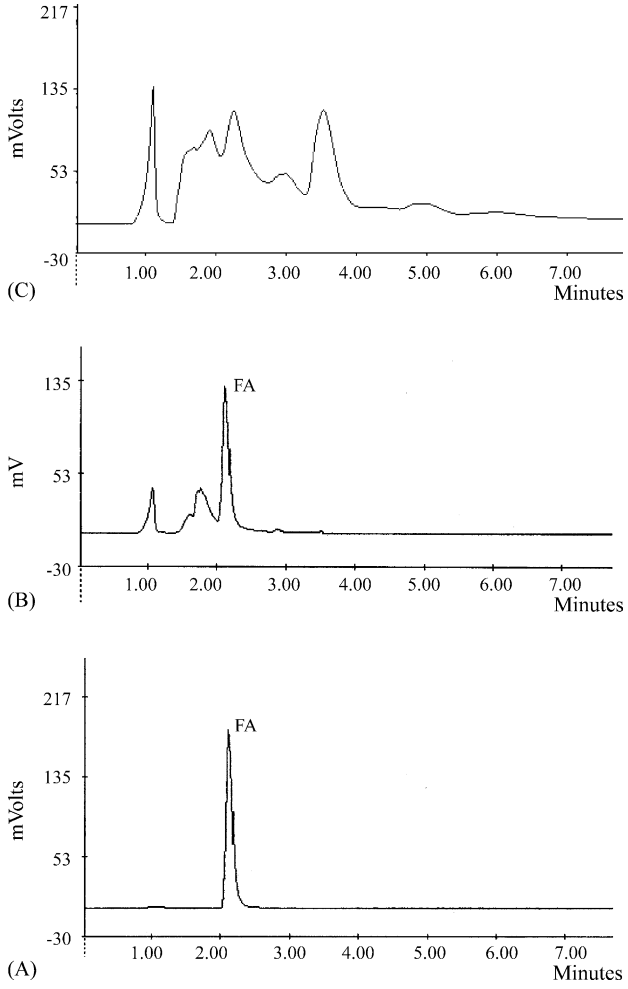

Fig. 3. Liquid chromatograms obtained for 44 mg l^{-1} FA standard solution (A), for FURAN1 resin solution (B) and for FENAC1 resin solution (C), detected at $\lambda = 220$ nm.

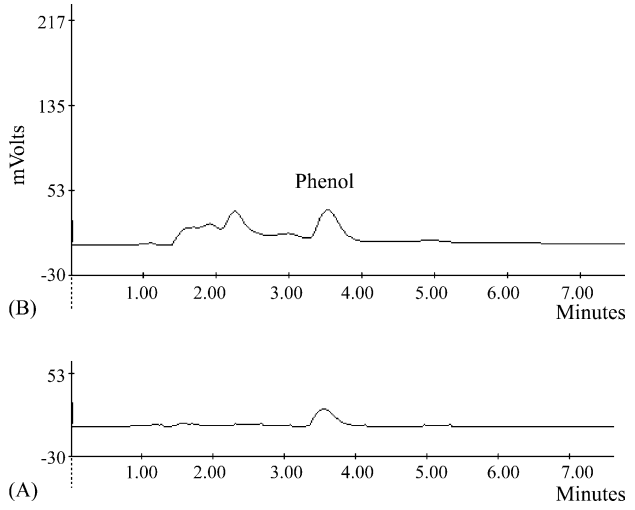

Fig. 4. Liquid chromatograms obtained for a mixture of 44 mg l^{-1} FA and 10 mg l^{-1} phenol (A) and for FENAC1 resin solution (B), detected at $\lambda = 273$ nm.

showed only a peak at 3.6 min for phenol (Fig. 4A). Chromatograms obtained with sample solution had similar configurations (Figs. 3C and 4B) using both wavelengths for FENAC1 solution, showing that interferent components are present in this resin. These interferents were also observed in the two other phenolic samples, not allowing the quantification of free FA in these resins. Nevertheless, for furanic resins LC method can be applied. It should be noted that formaldehyde is not visible at the wavelength considered (220 nm) and so it was not an interferent.

Table 1 presents the results express in mass percentage mean values of free FA content and respective recoveries for several resin samples. Relative standard deviation (R.S.D.) of the determinations ($n = 9$) and relative deviation (R.D.) between the results of the two methods are also shown. It can be observed that no free FA was detected for two of the phenolic resins and in FENAC2 it just appeared as a trace; this was the expected result considering the constitution of the resins studied. According to the results obtained, it can be concluded that both developed methodologies have a good precision (R.S.D. $\leq 7\%$) and very good recoveries (close to 100%). The relative deviation calculated for furanic resins showed that the results for both methods are in good agreement. GC method showed the advantage of a feasibility that did not depend on the resin characteristics. Nevertheless, as the time needed to perform two consecutive injections is smaller for LC than GC (latter method has the additional time of column cooling), according to the temporal efficiency, LC method is more advantageous when possible to apply.

Table 1
Mean values of free FA content in foundry resins and respective recoveries for GC and LC methods

Resin	GC		LC		R.D. (%)[b]
	FA (%, w/w)[a]	Recovery (%)[a]	FA (%, w/w)[a]	Recovery (%)[a]	
FURAN1	54 (±6)	103 (±8)	52.6 (±1)	96 (±2)	3
FURAN2	29 (±6)	101 (±3)	29.2 (±0.3)	107 (±0.3)	−0.6
FURAN3	72 (±6)	108 (±9)	72.7 (±0.1)	102 (±0.2)	−1
FENAC1	nd	101 (±4)	na	na	na
FENAC2	0.17 (±7)	104 (±8)	na	na	na
FENALC	nd	94 (±4)	na	na	na

nd: not detected; na: not applied.
[a] Relative standard deviation, R.S.D. in parenthese ($n = 9$).
[b] Relative deviation between the two checked methods.

4. Conclusions

The development of GC methodology provided an efficient and reproducible method for the determination of free FA in resin samples used in foundry industry. LC technique was also succeeded when applied to furanic resins. Nevertheless, the existence of interferents in the matrices hindered the use of this technique for phenolic resins. Although the complexity of the foundry resins, the sample pre-treatment selected was a simple extraction process, using methanol as solvent. It was concluded that the developed methods can be implemented in laboratories for routine analysis.

The limits of detection obtained make the developed chromatographic procedures applicable for environmental analyses of this pollutant in foundry waste sands, if associated with sample concentration techniques such as solid-phase extraction.

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