

QUANTITATIVE ANALYSIS OF PHENOL AND ALKYLPHENOLS IN BRAZILIAN COAL TAR

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The main purpose of this work is the identification and quantification of phenolic compounds in coal tar samples from a ceramics factory in Cocal (SC), Brazil. The samples were subjected to preparative scale liquid chromatography, using Amberlyst A-27™ ion-exchange resin as stationary phase. The fractions obtained were classified as “acids” and “BN” (bases and neutrals). The identification and quantification of phenols, in the acid fraction, was made by gas chromatography coupled to mass spectrometry (GC/MS). Nearly twenty-five phenols were identified in the samples and nine of them were also quantified. The results showed that coal tar has large quantities of phenolic compounds of industrial interest.

Keywords: coal tar; phenols; GC/MS.

INTRODUCTION

Coal is used in industries as a natural source of energy, mainly in gasification processes. An important by-product of the thermal treatment of this matrix is coal tar, considered today as an environmental by pollutant material¹. On the other hand, substances that have wide application in the chemical and pharmacological industries can be found in this matrix². Phenol and substituted phenolic compounds are widely used in the production of polymers, drugs, dyes, explosives, pesticides, stabilizers and antioxidants^{3,4}.

However, when phenolic compounds are discharged into the environment they can represent a serious hazard, mainly by the contamination of superficial and underground waters. Thus, at trace levels they can cause prejudice to the majority of the aquatic organisms and can induce bioaccumulation in the food chain^{4,6}. Phenolic compounds are also pointed out as important co-carcinogenic substances^{3,7}. They can considerably increase the effects of a secondary carcinogen (a substance that does not form cancerous tumors at the introduction point but in remote points and, sometimes, in specific organs).

The importance of co-carcinogenic properties of phenolic compounds is higher than that normally assigned to them, since some kinds of human cancer, due the exposition to certain materials, can result from small quantities of primary carcinogens (which promote animal cancers at the application point) and relatively higher quantities of co-carcinogens³.

The presence of phenolic compounds in the environment is preoccupying not only due to the knowledge of their dangerous facets but (maybe mainly) from some indications that these compounds can be genotoxic and there is a lack of enough data to discard with security, this possibility³.

Thus, the investigation of components of coal tar that can promote hazardous effects to human health and to the environment and, on the other side, the social and economic advantages that result from

industrial utilization of these compounds, where a decrease the costs of medical treatment, for example, must be carefully considered.

Coal is an alternative energy source that will assume a future key position with the decrease of oil production. The southern region of Brazil is an important coal producer and consumer, mainly in thermoelectric power plants. In spite of this, there is a lack of Brazilian work focusing on the phenolic composition of coal tar and its utilization as feedstock for other industries. In this work phenols were extracted by ion-exchange liquid chromatography and quantified by GC/MSD using the internal standard method.

EXPERIMENTAL PART

Coal tar samples were obtained from the ceramic industry Eliane (Cocal-SC/Brazil). Reagents and solvents utilized in this work were of p.a. grade, purchased from Merck S.A. The following standards (Sigma-Aldrich) were used: phenol, o-cresol, p-cresol, m-cresol, 2-ethylphenol, 2,5-dimethylphenol, 4-ethylphenol, 2,3-dimethylphenol, 3,4-dimethylphenol. 4-n-propylphenol was used as internal standard.

Resin treatment

10 g of Amberlyst A-27™ resin (Sigma-Aldrich) were mixed with 50 mL of a mixture of NH₄OH and methanol diluted in methanol (1+9, v/v). This mixture was stirred for 3 min and, after a few minutes at rest, the resin was washed in a sintered glass funnel with the following solvents: methanol (25 mL), water (until pH 7), acetone (25 mL) and n-hexane (25 mL).

Sample fractionation

200 mg of the coal tar sample were dissolved in dichloromethane. This solution was placed at the top of a glass column (15 cm long x 11 mm i.d.) packed with 10 g of Amberlyst A-27™ ion-exchange resin previously treated as described above. The basic and neutral compounds were eluted with 60 mL of n-hexane and the acidic fraction (phenolic compounds) was eluted with 70 mL of a mixture

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of formic acid/diethyl ether (1+6 v/v). The acidic fraction was dried with anhydrous sodium sulfate and its volume was reduced to 1 mL under a gentle steam of ultra-pure nitrogen. The acid fraction was derivatized with bis-trimethylsilylacetamide (BSA)⁸ to improve the chromatographic performance of the phenolic compounds⁹⁻¹². The extraction procedures were made in triplicate and each acid fraction was injected three times (resulting 9 injections) in the GC/MS system (SCAN mode). These injections were made for specify the single ions for the quantitative analysis (SIM mode).

Quantitative analysis

Individual stock solutions were made with each standard phenolic compound at 1,000 mg L⁻¹ in dichloromethane. The standard compounds were at least 99% pure. A spike solution (also in dichloromethane) at 100 mg L⁻¹ of all the standards was made from the stock solution. An aliquot of this spike solution was submitted to the extraction process and 1 µL of the extracts were injected in the GC/MS system, for recovery calculations. Real samples were not used for recovery tests. All the experiments were made in triplicate. The GC/MS analysis conditions are described in Table 1.

Table 1. GC/MSD analysis conditions

Parameter	Condition
temperature program	70°C – 1 °C/min – 100 °C
Injection mode	Splitless
Column head pressure	12 psi
Column	HP-5 (30 m x 0.20 mm i.d. x 0.11 mm film thickness)
Equipment	GC/MS HP – 5988 A
Ionization mode	Electronic impact at 70 eV
Carrier gas	Helium
Flow rate	1mL/min

RESULTS

Figure 1 presents the Total Ion Current (TIC) chromatogram for the samples acid fraction. The identification of the numbered peaks is presented in the Table 2.

Twenty-three phenols were tentatively identified, as their trimethylsilyl derivatives; nine of them had their identities confirmed by co-injection of standards.

The recoveries of phenols ranged from 59.9% for phenol to 99.9 % for 4-ethylphenol, while the detection limit varied from 3 to 12

mg kg⁻¹ (Table 3). The low recovery of phenol can be explained by its high volatility.

The amount of phenols in the samples varies from 8.13 mg kg⁻¹ for 2-ethylphenol to 190.70 mg kg⁻¹ for 4-ethylphenol (Table 3).

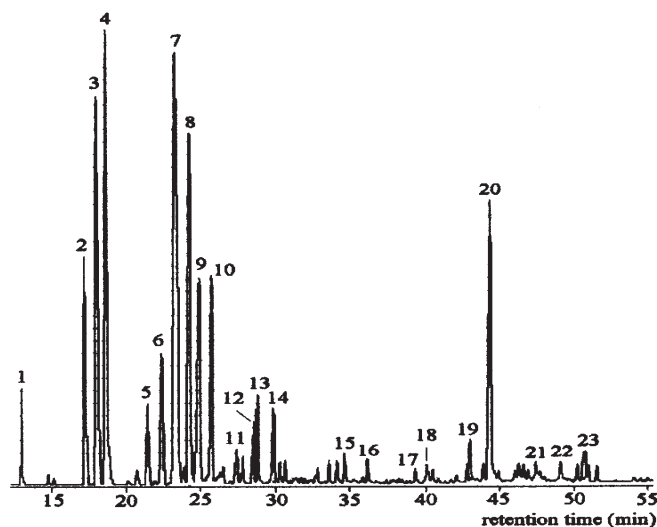


Figure 1. TIC chromatogram of the phenolic compounds in coal tar extract

Table 2. Identification of the numbered peaks in the GC/MSD (SCAN mode) chromatogram

# Peak	Compound	Identification method
1	phenol	MS, standard
2	o-cresol	MS, standard
3	m-cresol	MS, standard
4	p-cresol	MS, standard
5	2-ethylphenol	MS, standard
6	2,5-dimethylphenol	MS, standard
7	2,6-dimethylphenol	MS
8	4-ethylphenol	MS, standard
9	2,3-dimethylphenol	MS, standard
10	3,4-dimethylphenol	MS, standard
11,12,13,14	C ₂ -phenol	MS
15,16	C ₃ -phenol	MS
17,18	C ₄ -phenol	MS
19	1-naftol	MS
20	2-naftol	MS
21,22,23	C ₁ -naftol	MS

Table 3. Quantification results of phenolic compounds in the sample

Compound	Detection limit (mg kg ⁻¹)	Recovery (%)*	Concentration in the sample (mg kg ⁻¹)	Selected ions
phenol	3	59.9 ± 1.9	45.55 ± 0.86	94, 166
o-cresol	3	67.3 ± 0.7	35.73 ± 0.25	108, 180
m-cresol	5	70.4 ± 1.4	66.63 ± 0.93	108, 180
p-cresol	5	80.1 ± 1.6	73.35 ± 1.17	108, 180
2-ethylphenol	5	94.1 ± 0.5	8.13 ± 0,04	122, 194
2,5-dimethylphenol	5	69.8 ± 0.3	13.43 ± 0.04	122, 194
4-ethylphenol	12	99.9 ± 19.9	190.70 ± 37,94	122, 194
2,3-dimethylphenol	12	70.7 ± 0.1	15,84 ± 0.01	122, 194
3,4-dimethylphenol	12	84.6 ± 0.3	16.30 ± 0,05	122, 194

* For the standard mixture at 100 mg L⁻¹

CONCLUSIONS

The results of the quantitative analysis demonstrate that the methodology adopted is simple and adequate for enrichment of phenolic compounds in this kind of sample.

The quantities of phenols compounds found in the samples justify their extraction for utilization as feedstock for the drug, paint, dye and other chemical industries, mainly with respect to phenol, the cresol isomers and 4-ethylphenol, that are the predominant phenols in the samples.

The extraction of these compounds from coal tar samples, in the future, will permit a decrease in feedstock material importation, resulting in a reduction in manufactured product costs as well in environmental preservation.

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