

## Preliminary characterization of anhydrous ethanol used in Brazil as automotive fuel

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### Abstract

This work reports preliminary studies on the characterisation of anhydrous ethanol (AEA) used as an automotive fuel mixed with gasoline in Porto Alegre (South Brazil). Pre-concentration of the impurities contained in 1000 ml of AEA was carried on through solid-phase extraction using XAD-4™ resin. The main compounds in the extract were identified by means of spectral data from the library of the equipment. The concentrate was then fractionated using a preparative liquid chromatographic column filled with activated silica gel and the elution procedure was carried out with, *n*-hexane, *n*-hexane–benzene (1:1, v/v) and dichloromethane. Prior to analysis by GC–MS, each fraction was reduced to 1 ml with a gentle stream of nitrogen. Saturated linear hydrocarbons and aromatic hydrocarbons eluted in the first fraction and oxygenated compounds such as aldehydes, ketones and alcohols, eluted in the second one, were the main compounds detected in the sample.

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**Keywords:** Preparative chromatography; Fuel; Ethanol

### 1. Introduction

Since 1917, anhydrous ethanol (AEA) is used, pure or mixed with gasoline, as an automotive fuel [1]. In Brazil, several percent amounts of AEA have been added to gasoline since then, following the policy of the Brazilian government related to fuel requisites. Its continued use is due to the extensive sugar cane culture existing in Brazil, thus characterising a renewable energy source at low cost. Presently, the allowed AEA amount added to gasoline is around 24% [2]. Ethanol and other

oxygenates such as methanol, propanol, butanol and methyl *tert*-butyl ether (MTBE) are blended with gasoline also in the USA and in several other countries. They are used as octane enhancers in the place of toxic tetraethyl lead and as reducers of CO emissions by enleaning the fuel to air mixture. Limits to the content of oxygenates in gasoline are related to corrosion, economic and environmental concerns (CO and ozone emission, NO<sub>x</sub> and formaldehyde formation) [3].

The solvent properties of ethanol (EtOH) are very similar to those of water, excepting the higher ionic dissociant power of the latter. Both water and ethanol are amphiprotic solvents, EtOH being slightly less acidic and less basic than water. Due to this similarity, methods for pre-concentrating organic

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and/or inorganic impurities in water are expected to be used quite successfully in AEA characterisation [4].

The most convenient and popular technique for pre-concentration is solid-phase extraction (SPE). It involves most frequently the passage of a large volume of sample through a small packed bed containing a solid reagent, which binds preferentially the analyte. This is followed by the passage of a suitable eluent, which then releases the concentrated analyte [5].

Among polymeric sorbents, the most widely used are the styrene–divinylbenzene copolymers, which present a hydrophobic surface. They are characterised by a broad pH-stability range, present a high surface area per gram and are relatively selective for analytes with aromatic rings such as triazine, phenol and other polar aromatic compounds, due to specific  $\pi$ – $\pi$  interactions [6,7]. Therefore, trace organic contaminants such as weak acids and bases and neutral compounds can be extracted quantitatively from water with polystyrene–divinylbenzene resins such as XAD-4™ [8].

In spite of the increasing use of AEA blended with gasoline in Brazilian automobiles, there are few data on the composition of the commercial AEA, as well as on its combustion residues. Preliminary studies on the characterisation of commercial AEA produced from sugar cane are reported in this study. A solid-phase extraction method employing an XAD-4 resin to concentrate the impurities present in AEA is described. This step is followed by a preparative liquid chromatography in order to fractionate the impurities, which are then characterised by gas chromatography–mass spectrometry (GC–MS) analysis.

## 2. Experimental

### 2.1. Reagents and samples

A polystyrene resin, XAD-4 from Sigma (St. Louis, MO, USA), was used in the present study. The resin is characterised by a surface area of 750 m<sup>2</sup> g<sup>-1</sup>, 20–50 mesh beads and an average pore diameter of 50 Å and it was purified before use in a Soxhlet apparatus, first with acetone and then with

methanol. Silica gel, anhydrous reagent grade sodium sulphate and analytical grade solvents were purchased from Merck (Darmstadt, Germany).

Before use, sodium sulphate was heated overnight at 300 °C and silica gel (0.063–0.200 mm pore diameter and 70–230 mesh beads) was activated at 140 °C for 4 h, both reagents being stored into cleaned glass bottles inside a desiccator. All solvents used as eluents were bi-distilled and samples of anhydrous ethanol were kept under refrigeration at 4 °C.

### 2.2. Analytical procedures

#### 2.2.1. Pre-concentration

One gram of XAD-4 was packed into a glass column (15×1 cm) and washed with 50 ml of dichloromethane. One liter of the anhydrous ethanol sample was then passed through the resin bed at a 5 ml min<sup>-1</sup> rate to allow the adsorption of impurities. The adsorbed compounds were then released with three 5 ml aliquots of dichloromethane and the extract (a mixture of the three aliquots) was dried by passing it through another 15×1 cm column packed with 6 g of anhydrous sodium sulphate. The final volume of the extract was then reduced to 1 ml using a gentle nitrogen stream at room temperature (20 °C) before both total ion chromatogram analysis and fractionation with silica.

#### 2.2.2. Chromatographic separation

A preparative liquid chromatographic column filled with 3 g of activated silica gel, over which 0.5 g of sodium sulphate were placed, was washed with 15 ml of bi-distilled *n*-hexane. The 1 ml extract resulting from the pre-concentration step was then mixed with 500 mg of activated silica gel and added to the chromatographic column. Fraction 1 was then eluted with 10 ml of bi-distilled *n*-hexane, Fraction 2 was eluted with 20 ml of *n*-hexane–benzene (1:1, v/v) and the last fraction (Fraction 3) was obtained by elution with 20 ml of bi-distilled dichloromethane. All fractions were reduced to 1 ml by using a gentle stream of nitrogen (200 ml min<sup>-1</sup>) at room temperature, prior to the analysis by GC–MS.

#### 2.2.3. Acquisition of GC–MS data

GC–MS data analysis was performed with a

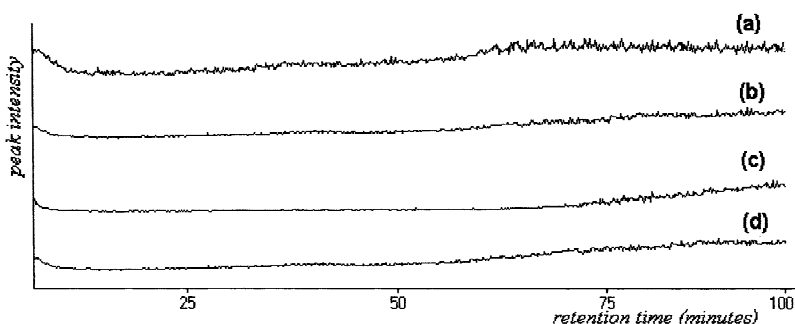


Fig. 1. Total ion chromatogram of ethanol (analytical-reagent grade) blanks: (a) XAD-4 extract before chromatographic fractionation; (b) Fraction 1 from the silica gel preparative liquid chromatography; (c) Fraction 2 from the silica gel preparative liquid chromatography; and (d) Fraction 3 from the silica gel preparative liquid chromatography. Experimental conditions are described in the text.

Shimadzu QP5050A instrument using a 0.25 mm internal diameter HP-1 capillary column (HP, Palo Alto, CA, USA) 60 m long with a 0.25  $\mu\text{m}$  film thickness. The operational conditions were the following: initial column temperature, 50  $^{\circ}\text{C}$ ; hold for 2 min; heating from 50  $^{\circ}\text{C}$  to 75  $^{\circ}\text{C}$  at 1  $^{\circ}\text{C min}^{-1}$ ; hold for 2 min; heating from 75  $^{\circ}\text{C}$  to 300  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C min}^{-1}$ ; hold for 40 min. The volume of the samples was 1  $\mu\text{l}$ , injected in the split mode (1:20), the injector temperature being 250  $^{\circ}\text{C}$ , the column flow 1  $\text{ml min}^{-1}$  and the source temperature 280  $^{\circ}\text{C}$ . A mass scan range from 35 to 500 u at 0.83 scans  $\text{s}^{-1}$  was used with a 1000 scan threshold and an electron energy of 70 eV.

#### 2.2.4. Blank analysis

In order to avoid artefacts originated from the method, solvents or adsorbents, the whole procedure was applied to a sample of ethyl alcohol p.a., which

was taken as the sample blank. The fractions obtained from the blank were then analysed by GC–MS following the same procedure as described for the sample.

### 3. Results and discussion

Fig. 1 shows the chromatograms for the blank analysis. This result evidences that there are no compounds that can be attributed to any contamination in the system, neither in the XAD-4 pre-concentration nor in the silica gel fractionation steps.

The total ion chromatogram of the extract obtained with XAD-4 by SPE, before the fractionation with silica, is shown in Fig. 2. The main compounds tentatively identified by means of spectral data from the library of the equipment were linear saturated hydrocarbons that are labelled by a capital “C”

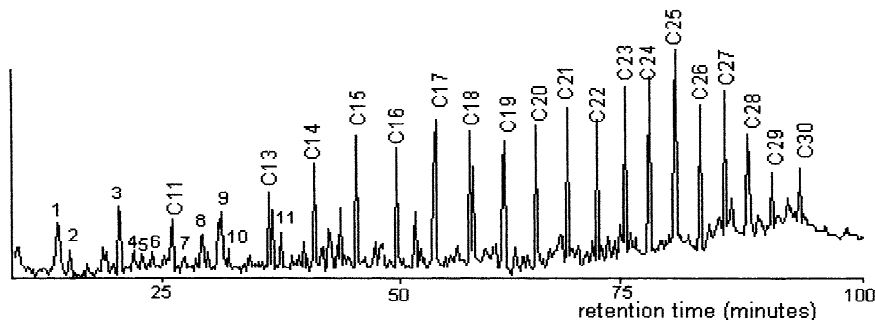


Fig. 2. Total ion chromatogram of the anhydrous ethanol XAD-4 extract before chromatographic fractionation. Experimental conditions are described in the text.

Table 1  
Peak identification of Fig. 2

Peak	Identification	Peak	Identification
1	<i>o</i> -Xylene	7	C <sub>4</sub> Benzene <sup>a</sup>
2	<i>m</i> -Xylene and <i>p</i> -xylene	8	Naphthalene
3	Isopropylbenzene	9	1 Methyl-naphthalene
4	<i>n</i> -Propylbenzene	10	2 Methyl-naphthalene
5	C <sub>3</sub> Benzene <sup>a</sup>	11	Dimethyl-naphthalene
6	Indane		

<sup>a</sup> Alkyl substituents with *n* carbon atoms, *n*=3 or 4.

followed by a digit which indicates the number of carbon atoms in the molecule. Some aromatic hydrocarbons are also identified in this sample, as shown in Table 1. Other compounds present in the sample at very low concentration could not be identified.

Figs. 3 and 4 show, respectively, chromatograms of fractions 1 and 2, obtained from the XAD-4 extract by applying the preparative liquid chromatographic fractionation technique. The marked peaks

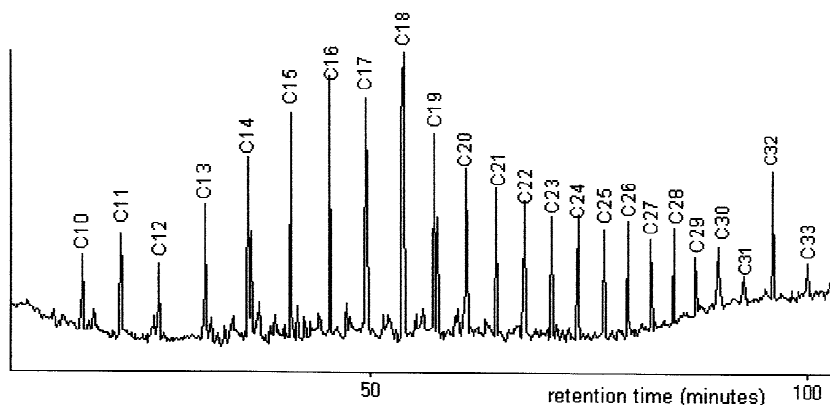


Fig. 3. Total ion chromatogram of Fraction 1 of the anhydrous ethanol XAD-4 extract. Experimental conditions are described in the text.

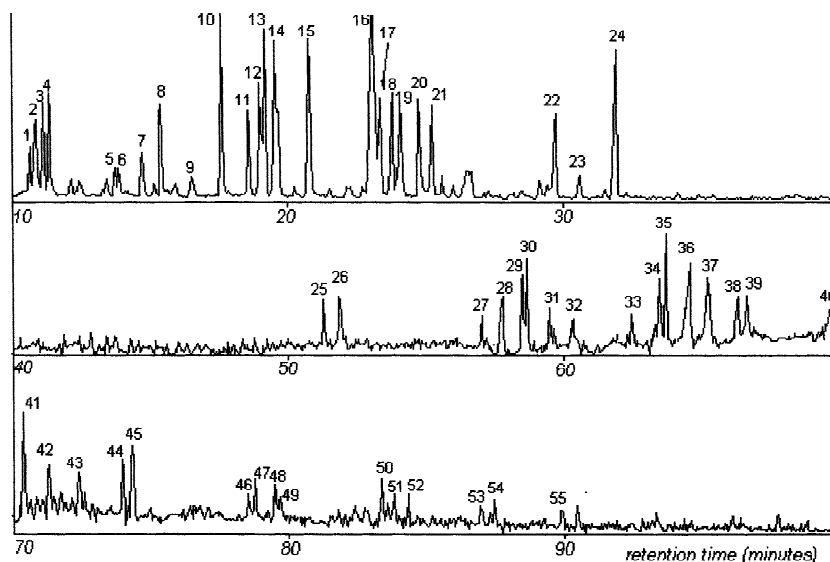


Fig. 4. Total ion chromatogram of Fraction 2 of the anhydrous ethanol XAD-4 extract. Experimental conditions are described in the text.

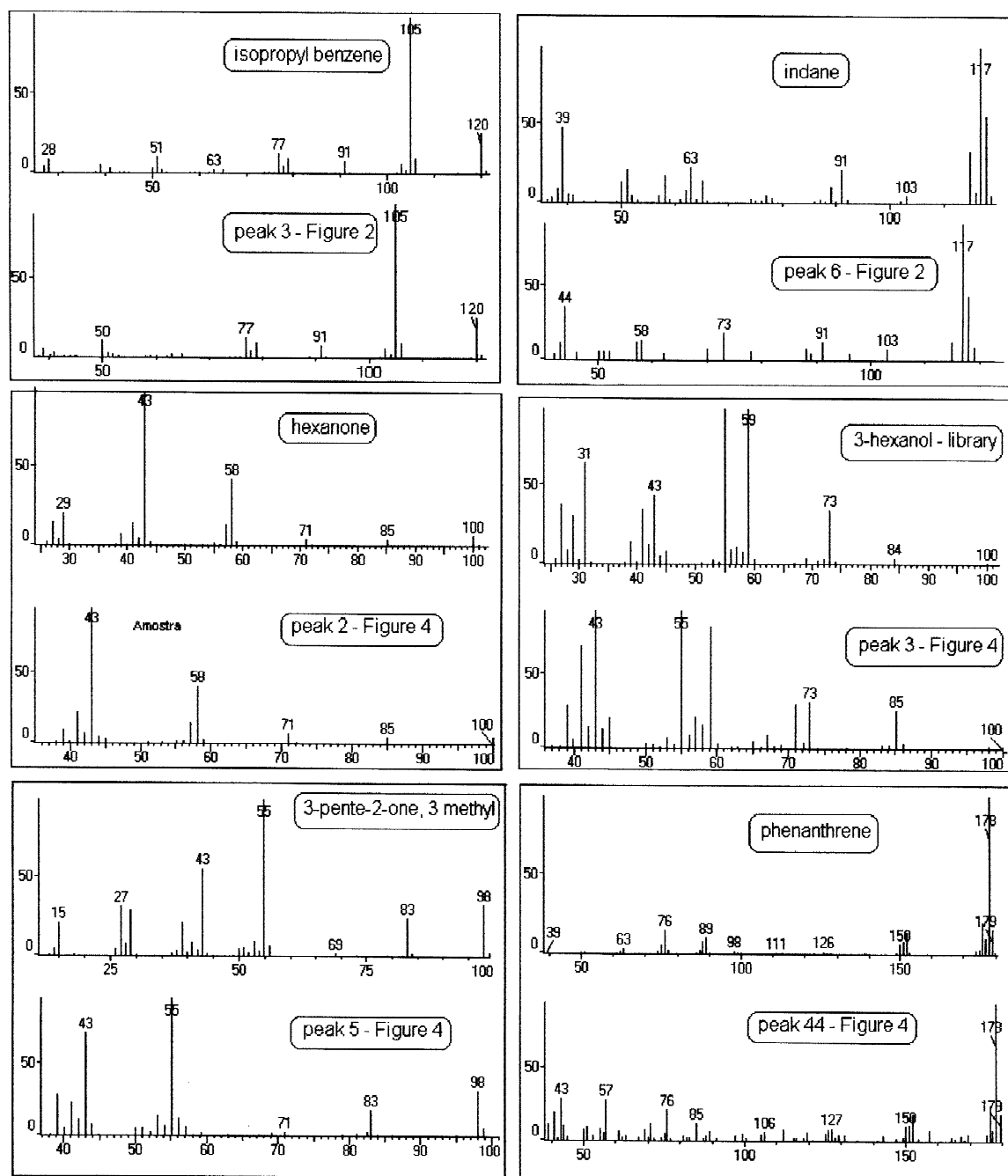


Fig. 5. Comparison of some spectra of identified compounds and the corresponding spectra from the equipment library.

Table 2  
Peak identification of Fig. 4

Peak	Identification	Peak	Identification
1	<i>n</i> -Heptane	19	Hexanone, dimethyl
2	Hexanone	20	Hexadienal
3	Hexanol	21	Pentanone, methylene
4	Heptanol	22	Pentadiene, dimethyl
5	Pentenone, methyl	23	Heptenone
6	Pentanone, methylene	24	Pentadiene, dimethyl
7	Hexadienol	25,25	Methylnaphthalene
8	Pentene, dimethyl	27–32	Dimethyl- or ethylnaphthalene
9	Hexadienol	33–37	Trimethyl- or methyl/ethylnaphthalene
10	Pentynol, methyl	38	Fluorene
11	Hexynol	39	Trimethyl- or methyl/ethylnaphthalene
12	Pentynone	40–43	C <sub>4</sub> -Naphthalene <sup>a</sup>
13	Hexanone, dimethyl	44	Phenanthrene
14	Pentynol, methyl,	45	Anthracene
15	Butanol, ethyl	46–49	Methylphenanthrene or methylanthracene
16	Hexynone, dimethyl-	50–52	C <sub>2</sub> -Phenanthrene or C <sub>2</sub> -anthracene <sup>a</sup>
17	Pental	53–55	C <sub>3</sub> -Phenanthrene or C <sub>3</sub> -anthracene <sup>a</sup>
18	Pentenone, methyl		

<sup>a</sup> Alkyl substituents with *n* carbon atoms, *n*=2, 3 or 4.

are identified in Table 2 while the linear saturated hydrocarbons are identified in Fig. 2 by a capital “C” and an index that corresponds to the number of carbon atoms in the molecule. The chromatographic analysis of Fraction 3 did not show any peak that is the reason why it is not presented here. Finally, Fig. 5 compares spectra of some of the identified compounds and the corresponding spectra available from the library (Wiley) of the equipment.

These results show that practically all saturated hydrocarbons were eluted in Fraction 1 while some aromatic and oxygenated compounds were found in Fraction 2. The main oxygenated compounds recovered in Fraction 2 were aldehydes, ketones and alcohols. Substances recovered in Fraction 3 presented a bad chromatographic profile with low resolution.

#### 4. Conclusions

The results indicate that the use of XAD-4 resin allows the separation of impurities from AEA. The saturated hydrocarbons and the most part of aromatic compounds are eluted in Fraction 1, oxygenated compounds such as aldehydes, ketones and alcohols

are found in Fraction 2 and substances removed in Fraction 3 present low chromatographic resolution.

It is seen that the organic impurities found in AEA do not represent severe problems for its use as a fuel. However, due to the presence of aldehydes and ketones, it is necessary to evaluate the environmental impact associated to the use of this product.

The majority of the compounds in the sample are linear saturated hydrocarbons. However, a significant number of compounds were not identified due to their very low concentration.

#### Acknowledgements

We acknowledge FAPERGS, CNPQ, FINEP and CTPETRO for support.

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