Determination of methanol and ethanol by gas chromatography following air sampling onto florisil cartridges and their concentrations at urban sites in the three largest cities in Brazil

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Abstract

A new sampling protocol was developed to determine methanol and ethanol in the gas phase, at low concentration levels, in urban atmospheres. The procedure involves collection of air samples (20.0–30.0 l) with three florisil cartridges connected in series, at a flow rate ranging from 1.0 to 2.0 l min\(^{-1}\) and subsequent elution of the alcohols with water. Separation and quantification were done by gas chromatography (GC) coupled with a flame ionization detector, ‘SPI’ injector and column DB WAX (30 m × 0.53 mm × 1 μm). The minimum mass detected by the method, based on two times the average background mass on the blank cartridges, was 0.3 μg for both alcohols which, for a sampled volume of 30 l, resulted in detection limits of 7.6 and 5.3 ppbV for methanol and ethanol, respectively. The determined alcohol concentrations, in 42 different samples from the three largest cities in Brazil—São Paulo, Rio de Janeiro and Salvador—ranged from 72 ppbV to below the detection limit for methanol and from 355 to 12 ppbV for ethanol. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Atmospheric methanol; Atmospheric ethanol; Sampling

1. Introduction

In the last two decades, the use of oxygenated fuels, like methanol and ethanol, pure or mixed with gasoline, has been growing due to the benefits of improved air quality and also for economic reasons. In Brazil, the number of light duty vehicles powered by pure hydrated ethanol is estimated at about 4 million [1–3], while the remaining vehicles actually utilize a mixture (22:78 v/v) of ethanol:gasoline. This results in an increase of alcohol emissions to the atmosphere in at least two ways: evaporation and as unburned fuel. Therefore, there is a need for the development of analytical procedures to determine these...
compounds in the atmosphere, at low concentration levels, in order to permit an evaluation of possible impacts from their emissions on formation of chemical species in the atmosphere, such as ozone, aldehydes, carboxylic acids and other photochemical oxidants [4,5]. Unfortunately, there is very little information in the literature regarding analytical protocols for alcohol sampling at low concentration levels. Due to these low concentrations, the air volumes required to determine, in a quantitative way, the atmospheric levels of methanol and ethanol, are frequently in the range of several liters. Classical sample collection into glass impingers containing water is difficult and troublesome for handling during field campaigns, while the commonly used solid sorbents present very low breakthrough volumes for both compounds [6]. In fact, most of the analytical methods reported were developed for alcohol determination in vehicle exhaust [7–10] or alcoholic beverages [11–18]. In both cases the determinations involve high concentration levels.

The present work compares the use of water and three solid sorbents (silica, basic alumina and florisil) in terms of efficiency of collection for atmospheric methanol and ethanol, taking into account the breakthrough volumes for each. Florisil cartridges showed, among the collection media evaluated, the best mean results for methanol and ethanol sampling. Thus, this system was tested in real sites, by means of atmospheric determination of ethanol and methanol in urban places in Rio de Janeiro, São Paulo and Salvador. The first results of alcohol concentrations in these cities are reported here.

2. Experimental

2.1. Material

The following were used: Tedlar and Teflon bags (80 l; BGI); Teflon chamber, transparent to sunlight, (3.5 m³); flowmeters; SEP-PAK (Millipore) solid sorbent cartridges: silica (80 µm × 690 mg × 30 mm × 9 mm i.d.), alumina (175 µm × 1850 mg × 27 mm × 9 mm i.d.) and florisil (125 µm × 900 mg × 24 mm × 9 mm i.d.); glass impinger; Teflon and silicone tubes; ethanol, methanol and acetonitrile, analytical grade (Merck); water, distilled and further purified in an E-Pure (Altech) system; and ‘zero’ gases (nitrogen, air, helium).

2.2. Equipment

The following were used: gas chromatograph (Varian 3400), equipped with flame ionization detector and ‘SPI’ injector; DB WAX column (30
Table 1  
Calibration curves for GC determination of methanol and ethanol \([H = aC + b]^a\)  

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>(a ; (\text{l mg}^{-1}))</th>
<th>(b)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2666</td>
<td>3.95</td>
<td>0.9992</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1938</td>
<td>3.5</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

\(^a\) \(a\), slope \((\text{l mg}^{-1})\); \(b\), intercept; \(C\), concentration \((\text{mg} \text{ l}^{-1})\); \(H\), peak height; \(r^2\) = correlation coefficient.

Limits of 7.6 and 5.3 ppbV for methanol and ethanol, respectively.

All cartridges, prior sampling, were pre-conditioned by elution with water (5 ml) and acetonitrile \((\text{MeCN})\) (5 ml), followed by partial dryness passing helium or nitrogen throughout. Methanol \((\text{MeOH})\) and ethanol \((\text{EtOH})\) standard atmospheres were obtained by injection, with a microsyringe, into the bags, of known amounts \((1 \text{ or } 10 \mu\text{l})\) of the respective alcohol using a ‘zero’ air flux as carrier gas \((2.0–3.0 \text{l min}^{-1})\), which, in turn, was used to fill the bag with specific air volumes \((\sim 70 \text{l} \text{ for small bags and } 1000–2000 \text{l for Teflon chamber})\). The exact concentration of methanol or ethanol, in each experiment, was determined taking into account the mass of alcohol put into the bag and the air volume used in dilution.

2.4. Breakthrough tests

For breakthrough tests, a known amount \((6.8 \mu\text{g})\) of \(\text{MeOH}\) or \(\text{EtOH}\) was collected on columns or impingers containing purified water, by means of a fixed volume \((0.60 \text{l})\) of standard atmosphere withdrawn from the Tedlar bag. Then, the columns or impingers were exposed to a ‘zero’ air flow, at \(1 \text{l min}^{-1}\), for variable periods, ranging from 0 to 75 min, one column or impinger for each time period. The air flow rate was controlled by a mass flowmeter, which was previously calibrated against a standard. After this time passing ‘zero’ air throughout, the column was eluted with 5 ml of water to a volumetric flask \((10 \text{ ml})\) and the volume taken up. A 1.0-\(\mu\text{l}\) aliquot of this solution was injected and analyzed by GC. When using water as collection medium, an aliquot \((1 \mu\text{l})\) of the total volume \((10 \text{ ml})\) was directly injected into the chromatograph immediately after each period passing ‘zero’ air. The scheme for alcohol sampling from the bag is shown in Fig. 2.

2.5. Samplings from bags, indoor, outdoor and urban atmospheric air

Samples were collected from Teflon bags \((80 \text{l})\) and Teflon chamber \((3.5 \text{ m}^3)\), with concentrations ranging from 15 to 74 ppbV for methanol and
Fig. 3. Ethanol fraction still retained, as function of the sampling system and zero air volume through it.

from 10 to 51 ppbV for ethanol, from two sites inside the laboratory, outside the building of the Institute of Chemistry, and at urban sites in Salvador, Rio de Janeiro and São Paulo. The flow rates ranged from 1.0 to 2.0 l min⁻¹ and final volumes from 30.0 to 60.0 l for samples collected from bags, inside and outside the laboratory, while for urban atmospheric samples final volumes were 20.0 or 30.0 l. In all cases, three cartridges connected in series were used. The air flow rate was controlled in the same way as described above. The cartridges were then eluted with 3 ml of water to a volumetric flask. The volume of water used for elution was set at this time at 3 ml in order to exceed the hold-up volumes of cartridges (between 1.6 and 1.8 ml), and give a maximum sensitivity to detector responses. The efficiency of recovery for the compounds was checked by a second elution (3 ml) over 10% of each sample lot. A 1.0-µl aliquot of the solution was injected and analyzed by GC. The interior of the laboratory and urban sites which were studied, are briefly described below.

2.5.1. Laboratory

The facilities of our research group, a set of three rooms with a total area of around 120 m², consist of an instrumental lab, a sample treatment lab and a third room for offices and computers.

2.5.2. Garibaldi Av. (Salvador)

This avenue, close to a car park of the university, has six traffic lanes (three in each direction) and near the sampling site is heavily occupied by commercial buildings and medical facilities. The sea is about 1 km away. Samples were collected ~1.0 m above the ground.

2.5.3. Muniz Barreto St. (Rio de Janeiro)

This is a secondary way that connects Praia de Botafogo and S. Clemente St. It has two traffic lanes in a single direction and near the sampling site has many residential and commercial buildings, as well as schools and clinical offices. The Botafogo beach—inside Guanabara’s bay—is nearly 200 m away. Samples were collected ~1.0 m above the ground.
2.5.4. **Rebouças Av. (São Paulo)**

Located at Pinheiros, this avenue has six traffic lanes (three in each direction) and near the sampling site has residential, and commercial buildings and restaurants. The samples were taken from the 9th floor (≈ 30 m above ground level) of a residential flat.

3. **Results and discussion**

For a given compound, the breakthrough volume is defined as the volume of air or carrier gas, by unit mass of the sorbent, for which the compound retained into the sorbent cartridge begins to migrate away from it. This migration is a consequence of its partition equilibrium, between solid and gas phases, and is a function of sorbent and compound type, the compound concentration in the sample, the sampling temperature, the humidity of air, the air flow rate and flow velocity and the presence of other contaminants that can interfere with sampling. Volatile compounds, in general, have low breakthrough volumes \[6,10\].

The breakthrough tests with water, silica, basic alumina and florisil short columns were conducted in accordance with the experimental procedures previously described. The choice of the sorbents was based on their polarity, high activity grade and basic surface (basic alumina and florisil), which could enhance the interaction with alcohol molecules through the H atom in the OH group. The tests results are shown in Figs. 3 and 4, where a lack of data means that the experiment was not performed for that sampling media in that volume. For methanol (Fig. 4), neither of the three sorbents could retain its total mass for air volumes near to 15 l. At this volume, the relative mass of methanol that still remained in the florisil column (the sorbent showing the best results) was only 80% of the original. Silica and alumina presented lower performances than florisil. With 30 l of air passing through the column, mass still retained on these sorbents dropped drastically to a fraction equal to or below 20%. Water, on the other hand, still retained 52% of the original mass of methanol for an air volume of 60 l, while for florisil no methanol was detected at this volume. For ethanol (Fig. 3), florisil short columns showed

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*Fig. 4. Methanol fraction still retained, as function of the sampling system and zero air volume through it.*
the best results, being capable of retaining the totality of the alcohol for air volumes up to 60 l, and even 80% for 75 l. Florisil columns were then selected for the subsequent studies described below.

In order to evaluate the previously chosen sorbent, according to conditions closely related to real atmosphere samplings, the next test was to sample methanol or ethanol from larger air volumes (30–60 l) and concentrations near to the ones expected in the air, collected from Teflon bags (80 l) or Teflon chamber (3500 l), as described in Section 2. During these tests (ten), ethanol sampled was always observed in the first column or, at worst, in the second (one case), while for methanol, a significant number of experiments (five) showed migration up to the third column. These results are summarized in Figs. 5 and 6. Of the five experiments for which methanol migrated up to the third column, three were done with 60-l samplings at 1.1 l min\(^{-1}\), one with 40 l at 1.4 l min\(^{-1}\) and the other with 30 l at 1.8 l min\(^{-1}\). In this way, the breakthrough values for methanol in florisil cartridges seemed to be determined by the flow velocity, once higher air volumes correspond to lower flow rates and higher flow rates to lower air volumes. Ethanol, on the other way, seems to be indifferent to the flow rate and flow velocity, at least at the range studied, which was chosen to give shorter sampling periods. In this way, to address a quantitative sampling for methanol, it was necessary to collect lower air volumes at lower flow rates, or to use more than three columns, although the last alternative would produce a high backpressure in the vacuum pump.

Finally, the florisil cartridges were used in real atmospheric samplings, as a mean to evaluate possible interference from other air contaminants, over retention of methanol and ethanol by the sorbent. Results for concentrations of methanol and ethanol, measured inside and outside the lab and at urban sites, are given in Table 2. In all samples collected, the mass of methanol determined was predominantly at the third column, showing a strong migration. As consequence, results reported for this alcohol are only estimates of concentrations.

For ethanol, although migration had also occurred for 13% of the samples—probably due to competition for active sites with water and other organic compounds—the mass of this alcohol at
the third column, when present, was much lower than at first and second columns, showing a profile that makes it possible to predict that a fourth column should have ethanol at blank levels (≈ 0.3 μg). From the total of 53 samples, 52—or 98%—presented a quantitative retention for ethanol in the three cartridges, thus making florisil a good choice as a sorbent for its sampling in atmospheric air, especially if one takes it into account that common solid sorbents have very low breakthrough volumes for these compounds.

Breakthrough volumes at 20°C, reported for 11 sorbents used to collect organic compounds in atmospheric air [6,10,19] are in the range of 0.013–3.30 l g\(^{-1}\) for ethanol and 0.006–0.950 l g\(^{-1}\) for methanol. A unique exception was a carbon based sorbent, named Carbosieve SIII®, with reported values of 7.50 and 55.0 l g\(^{-1}\) at 20°C for methanol and ethanol, respectively [6]. Nevertheless, no information was available about water coadsorption interferences, a type of problem commonly associated with carbon based sorbents, as well as the efficiency of recovery of alcohols by elution with water. At present, our group have ordered this product and, as soon as we get it, these tests will be carried out.

4. Conclusions

Among the collection media evaluated, florisil showed, when sampling atmospheric methanol and ethanol, the best results besides presenting advantages including easy handling and field transportation. The breakthrough volumes presented, mainly for ethanol, are at least one order of magnitude higher than those for other common sorbents used for atmospheric air sampling. This is specially important if one considers the low atmospheric concentrations of methanol and ethanol.

The collection system chosen was then used for sampling indoor and outdoor sites at the Institute of Chemistry and urban sites in the three largest cities of Brazil: Rio de Janeiro, São Paulo and Salvador. At these urban sites, methanol and ethanol concentrations ranged, respectively, from 72 ppbV to below the detection limit, and from 355 to 12 ppbV. The largest mean concentration was detected for ethanol in Rio de Janeiro, namely 66.4 ppbV.

Samplings with florisil cartridges, followed by quantitation with GC-FID, were quantitative for ethanol in 52 of 53 collected samples. Meanwhile,
Table 2
Concentration of methanol and ethanol at the indoor, outdoor and urban sites

<table>
<thead>
<tr>
<th>Locale</th>
<th>Number of collected samples</th>
<th>MeOH (ppbV)</th>
<th>EtOH (ppbV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Inside the laboratory</td>
<td>06</td>
<td>99.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Outside the laboratory</td>
<td>05</td>
<td>&lt;7.6</td>
<td>&lt;7.6</td>
</tr>
<tr>
<td>Garibaldi Av. (Salvador)</td>
<td>21</td>
<td>25.4</td>
<td>&lt;7.6</td>
</tr>
<tr>
<td>Muniz Barreto St. (Rio)</td>
<td>12</td>
<td>25.4</td>
<td>&lt;7.6</td>
</tr>
<tr>
<td>Rebouças Av. (SP)</td>
<td>09</td>
<td>72.5</td>
<td>&lt;7.6</td>
</tr>
</tbody>
</table>

for methanol, the results are only an estimation of the real concentrations. For this alcohol, quantitative measurements should involve short volumes and lower flow rates to avoid its strong migration up to the third column.

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References