Development and validation of an analytical method for quantitative determination of carboxylic acids in air samplers

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Abstract

The aim of this article was to realize a method for the determination and separation of formic and acetic acids in air samplers. For this purpose, an analytical ion chromatography method was developed, optimized under various measurement conditions and then validated. Selectivity, linearity, limit of detection, limit of quantification, precision and accuracy of the method were determined for the validation process. The resulted method can separate and determine the interested compounds, is fast, simple to reproduce and involves low reagent’s costs.

Keywords: Carboxylic acids; acetic acid; formic acid; method validation; IAQ

1. Introduction

The indoor environmental quality is very important because it has an direct influence on the occupant’s comfort and productivity [1, 2]. One of the most harming indoor pollutants are VOC and formaldehydes. The volatile organic compounds (VOCs) and formaldehyde are organic chemicals that have a high vapor pressure at ordinary room temperature. These substances are used to manufacture and maintain building materials, furniture, maintenance products and personal care products [3].
However, VOCs released from the wood products has been a long-studied problem. It is important to control and decrease VOCs concentration used during the production stage. Along with the wood products, paints, finishes and cleaning products are emitting VOCs, such as toluene, benzene, formaldehyde [4]. These substances have been identified to be associated with asthma, nasopharyngeal cancer and multiple subjective health complaints [5]. The impact on the human health influenced international organism such as EU to set maximum values for the emissions of volatile organic compounds [4] and several air sampling strategies are proposed.

Based on the human perception the response regarding the small variation of temperature or relative humidity is not the same. Thus occupants can report a "dry sensation" or irritation of respiration system due to a polluted environment accusing air humidity variations [5]. VOC can be identified by occupants based on odor but in [6] there is presented that the occupants are not able to identify an odor source, because they are living in an environment with odors from non-natural sources. Therefore they are not able to identify the sources that have an impact on their health. Any questionnaires that are used to identify the sources might be involuntary partially completed.

The formaldehyde is a natural metabolic product of the human body, exposure to high-dose increases the risk of acute poisoning. The International Agency for Research on Cancer in 2006 stated that long exposure can lead to chronic toxicity and even cancer. Therefore it is needed to detect and limit the concentration of formaldehyde at source (product emission) and remove if the concentration is high. Formaldehyde levels between 0.1 and 0.5 ppm (0.12–0.6 mg/m3) are detectable by human senses, between 0.5 and 1.0 ppm (0.6–1.2 mg/m3) can cause eye irritation, and above 1.0 ppm (1.23 mg/m3) can irritate the nose and throat [7].

The scope of this article is to present an method to evaluate the indoor air quality based on the formaldehyde presence in the air. The assessment is based on the concentration of formic and acetic acids. These acids are the results of the formaldehyde natural oxidation process.

2. Materials and methods

The analytical method develop for the separation and determinations of the two carboxylic acids (formic and acetic) was realized on a Dionex ICS-5000+ Ion chromatograph model, with integrated eluent generator, a conductivity detector and anion suppressor model 500 ORSA Dionex 2mm. To separate the acids, an IonPac AS-18 column chromatography coupled with a precolumns recommended by the manufacturer to determine anions and low molecular weight organic acids were used.

Elution mode was isocratic, and consisted of 10 mM of KOH as eluent. The thermostatic column was set at 20 °C and the injection volume was 5μl; the total running time of the method was 10 minutes.

The calibration curves were realized using external standard method. For this porpoise, analytical standards were purchase from LGC Standards, and consisted in 1000 mg/mL acetate and 1000 mg/mL formate.

3. Results and discussions

The results presents the method validation. The method’s parameters determine for the validation were: selectivity, linearity, limit of detection, limit of quantification, precision and accuracy.

The chromatographic columns plays an important role in the separation of chemical compounds. For this purpose, an IonPac AS-18 was chosen. This column have been described as being suitable for determination of low molecular weight organic acids like formic and acetic acids. IonPac AS Columns had been characterized in literature as having good results in separating formic and acetic acids and being able to determine this compounds in air samplers[8].

Along with the chromatographic column, the eluent concentration can make the difference between a good or an incomplete separation of the compound’s peaks. We started by testing different eluent concentrations on KOH, from 23mM to 2mM.

In Figure 1 is presented the two carboxylic acids with eluent concentration of 23mM KOH. In this case, the resolution between the peaks is lower than 2 and, as can be seen, the peaks are not completely separated at the base.
In Figure 1. Chromatogram of the carboxylic acids eluted with 23mM KOH.

Figure 2. Chromatogram of the carboxylic acids eluted with 2mM KOH.

Figure 2 presents the elution of the two carboxylic acids with eluent concentration of 23mM KOH. In Figure 2 the two peaks are completely separated, but, compared to the ones in the elution time is delayed and the analysis needs more time. To an easier comparison the retention time corresponding to 23mM KOH was 3.64 minutes for acetic acid and 3.90 minutes for formic acid, vs 10.99 for acetic acid and 14.02 for formic acid at 2mM KOH.

For this method, the most suitable elution concentration in terms of peaks separation and retention time, was chosen at 10mM KOH. The retention times can be seen in Table 1 and the chromatogram showing the peaks is presented in figure 3.

Fig. 3. Formic acid and acetic acid separation column IonPac AS 18
Table 1. Coefficient of determination and retention time for the formic and acetic acids.

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<th></th>
<th>Coefficients of determination</th>
<th>Retention time</th>
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<tr>
<td></td>
<td>(r²)</td>
<td>(minutes)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.999</td>
<td>4.36</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.999</td>
<td>4.98</td>
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</tbody>
</table>

After testing the height of the chromatographic peak for the same concentration for the two acids was concluded that formic acid gives an almost 2.5 higher peak than acetic acid. In order to have peaks in the same height range, the concentration of the calibration points were calculated to have concentration of acetic acid two times higher than acetic acid.

The calibration curves covered areas of work between 10 and 1000 μg/mL for acetic acid and 4 and 400 μg/mL formic acid. Six points were used for plotting each curve. The working standards were realized in low conductivity deionized water. All the working standards were realized by dilution from an intermediate standard consisting of 10000ug/L acetic acid and 4000ug/L formic acid.

Selectivity of the method was express as the resolution between the peaks of interest. A good resolution between the peak has to be higher than 2 between the peak of interest and the closest potential interfering peak. It was obtained a good resolution between the peaks of acetic and formic of 3.6, as given by the Chromleon 7 Software. The separation between the peaks can be seen in Figure 3.

The linearity of the method was evaluated in the concentration ranges of 4 to 400 μg/mL for formic acid and 10 to 1000 μg/mL for acetic acid. The theoretical concentration of each calibration point was plotted against the chromatographic signal from the detector. For each concentration three independent solutions were prepared. Good coefficients of determination were obtained greater than 0.995, as can be seen in table 1. The calibration curves obtain can be seen in Figure 4.

The precision of the method was express as Repeatability and was evaluated for a concentration of 200 μg/mL for acetic acid and 80 μg/mL for formic acid. The Repeatability obtained for acetic acid was 3.56 and for formic acid was 4.72.

The accuracy of an analytical procedure is the closeness of agreement between the conventional true value or an accepted reference value and the value found. For this method the Accuracy for acetic acid was 3.09 and for formic acid 4.25.

The limit of detection (LOD), characterized as the lowest detectable concentration, was determined as being the detector signal of a blank plus 3 times the standard deviation. LOD for acetic acid was at 0.65 μg/mL and for formic acid was at 0.25μg/mL.

The limit of quantification (LOQ), characterized as the lowest concentration that can be measurable, was determined as being the detector signal of a blank plus 10 times the standard deviation. LOD of this method for acetic acid was at 2.17 μg/mL and for formic acid was at 0.85μg/mL.
4. Conclusions

The method is suitable for the determination and quantification of acetic and formic acid with good separation of the two acids. It can be described as easy to reproduce, with or without an eluent generator due to its isocratic mobile phase. Also it doesn’t not implicate a lot of reagents, keeping the reagent’s cost low. Regarding time, the method takes only 10 minutes to determine the interested compounds.

References

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