A SIMPLE AND SOLVENT-FREE CHROMATOGRAPHIC METHODOLOGY FOR SIMULTANEOUS DETERMINATION OF METHANOL AND ACETIC ACID CONTENT OF POLYSACCHARIDES

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A simple and solvent-free methodology is proposed for the simultaneous determination of methanol and acetic acid released from polysaccharides. The methodology proposed involves the extraction of the analytes from headspace (HS) using a solid phase microextraction (SPME) technique, followed by separation of the analytes in a gas chromatograph with a flame ionization detector (GC-FID).

The SPME sampling parameters, such as coating fibre, time of extraction and effect of an interfering compound on the amount of the analyte extracted by the fibre were evaluated. Two types of SPME fibre coatings, PDMS and DVB/Carboxen/PDMS, were compared for their ability to extract methanol and acetic acid from sample headspace. Three times of extraction of the fibre exposure to the headspace were also studied (15, 30 and 45 min). Extraction during 30 min with DVB/Carboxen/PDMS fibre coating revealed to be the optimal experimental conditions for methanol and acetic acid extraction. In order to evaluate the effect of a possible interference of one analyte on the quantification of the other, calibration curves of each analyte were also constructed in the presence of two different concentrations of the other, 60 and 100 mg L^{-1} for methanol and 80 and 105 mg L^{-1} for acetic acid. Quantification of methanol and acetic acid were carried out using external calibration curves with concentration ranges between 40 and 100 mg/L and 25 and 105 mg/L, for methanol and acetic acid, respectively. No statistical differences (p<0.05) were observed among the three curves obtained for each compound, allowing to

conclude that during the extraction procedure with SPME, within this concentration range, no significant competitive interferences occur (Figure 1).

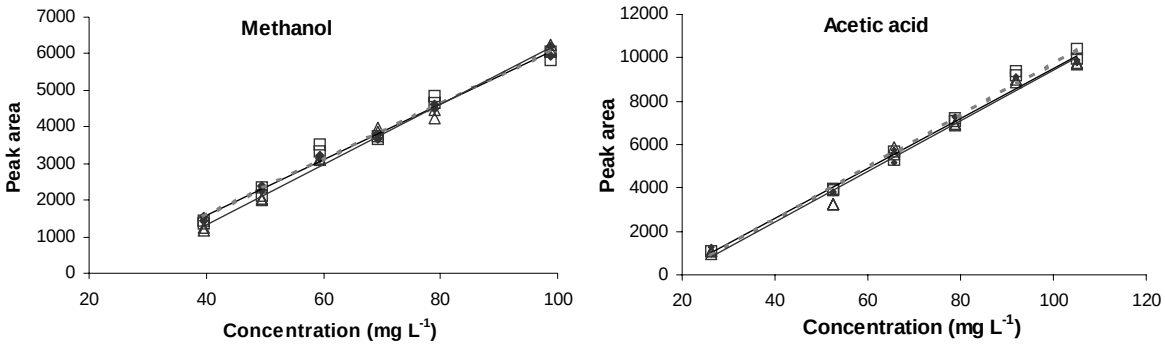

Figure 1. Calibration curves for methanol (no acetic acid (◆), 80 μg mL^{-1} acetic acid (□) and 105 μg mL^{-1} acetic acid (△)) and for acetic acid (no methanol (◆), 60 μg mL^{-1} methanol (□) and 100 μg mL^{-1} methanol (△)).

The optimised methodology was applied for determination of methanol and acetic acid contents released from a set of plum polysaccharides, which differ in their sugar composition, namely uronic acids (from 15 to 77 mol%) and total amount of sugars (between 562 and 997 mg/g). The values of methanol and acetic acid concentrations obtained were compared with those calculated from direct injection of the aqueous solution in a GC-FID (Waldron and Selvendran, 1990), since this methodology has been used for quantification of methanol and acetic acid content of polysaccharides. No statistical significant differences (p<0.05) were observed between the results obtained with the two methodologies. The proposed methodology has also revealed to be reproducible for determination of both methanol and acetic acid, since the errors were *ca*. 10% (expressed as percentage of the average).

The proposed HS-SPME-GC-FID methodology revealed to be simple, solvent-free and reproducible for the simultaneous determination of methanol and acetic acid content of polysaccharides, providing a considerable improvement in relation to most of methods used.

Reference:

Waldron K. W.; Selvendran R. R. (1990). Composition of the cell walls of different asparagus (*Asparagus officinalis*) tissues. *Physiol. Plant., 80*, 568-575.

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