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Pyrolysis-gas chromatography–mass spectrometry Kováts retention index of pyrolysis products of lignocellulosic materials

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ABSTRACT

Pyrolysis – gas chromatography – mass spectrometry (Py-GC–MS) is a common hyphenated analytical technique for the characterisation of lignocellulosic materials, but such natural polymers generate highly complex total ion current pyrograms. Recently, normalised retention time and automated deconvolution of chromatograms have been shown to be a viable method for analyses containing a large number of peak components. However, the use of Kováts retention index (RI) has not been examined in Py-GC–MS for lignocellulosic materials. In this study, we test the use of linear alkane polyethylene pyrolysis products to calibrate the Kováts RI for pyrolysis products of lignocellulosic materials in a Py-GC–MS system. Linear alkane polyethylene pyrolysis products yield a correct Kováts RI, which means the method has the advantages of being able to apply the NIST/EPA/NIH mass spectra library database for peak identification. In addition, using such an approach, Kováts RI of standard compounds calibrated using a GC–MS system may be used for structural certification of unknown pyrolysis products due to the similarities of RI calibration in both systems (GC–MS x Py-GC–MS).

1. Introduction

Pyrolysis is a common analytical technique for the characterisation of lignocellulosic materials, an important raw material for several industrial branches (e.g. pulp and paper, biorefinary an metallurgy), that use different products (e.g. cellulose, hemicellulose, lignin and charcoal) [1–11]. Pyrolysis of natural or synthetic products generates a set of complex mixtures of smaller pyrolysis product molecules. The composition of such molecules is related to the composition of the original sample, and due to their complexity, it is necessary to combine pyrolysis with other techniques such as gas chromatography and mass spectrometry (Py-GC–MS), to aid the separation and identification of the species produced by pyrolysis [12,13].

Natural polymers generate pyrograms with several peaks, and mass spectra and pyrogram libraries are only partially relevant to the interpretation of a substantial amount of peak data [14]. Until now the use of libraries has ignored the majority of the information available in the pyrograms, since peak identification has been based on mass spectra and retention time (RT) [15–19]. Various gas chromatography (GC) parameters influence the RT during Py-GC–MS analysis, such as the column length, film thickness, diameter, and size of the transfer line [20]; this represents a challenge for the identification of large numbers of compounds with similar mass spectra and slightly different RT. Recently, Smits et al. [21] used a normalised RT and automated deconvolution of pyrograms, providing a viable alternative method to ease the analysis of pyrograms with very complex peak-components.

It is known that the use of the retention index (RI) is more useful than using the RT for peak identification, since RI are quite independent of GC parameters. The temperature programming Kováts RI has been used for a long time [22,23], and a database using this index has been updated, making its use interesting for the identification of compounds resulting from a complex matrix [18,24,25,26]. The linear alkanes series (e.g. C_7–C_{40}) are usually used as reference standards to calculate the Kováts RI in GC–MS analysis. Therefore, the pyrolysis products of polyethylene (i.e. dienes, alkenes and alkanes [27]) should provide the linear alkanes needed to calculate the Kováts RI during pyrolysis analysis. A previous study has demonstrated the possibility of using polyethylene pyrolysis products for RI calibration and identification of pyrolysis products from paper pulp [14]. Herein we describe, for the first time, the use of polyethylene as a source of linear alkanes to calibrate the Kováts RI for Py-GC–MS analysis of lignocellulosic materials. The efficiency of the proposed methodology was validated by comparing the Kováts RI generated from lignocellulosic pyrolysis products with bio-oil compound Kováts RI calibrated using GC–MS analysis.

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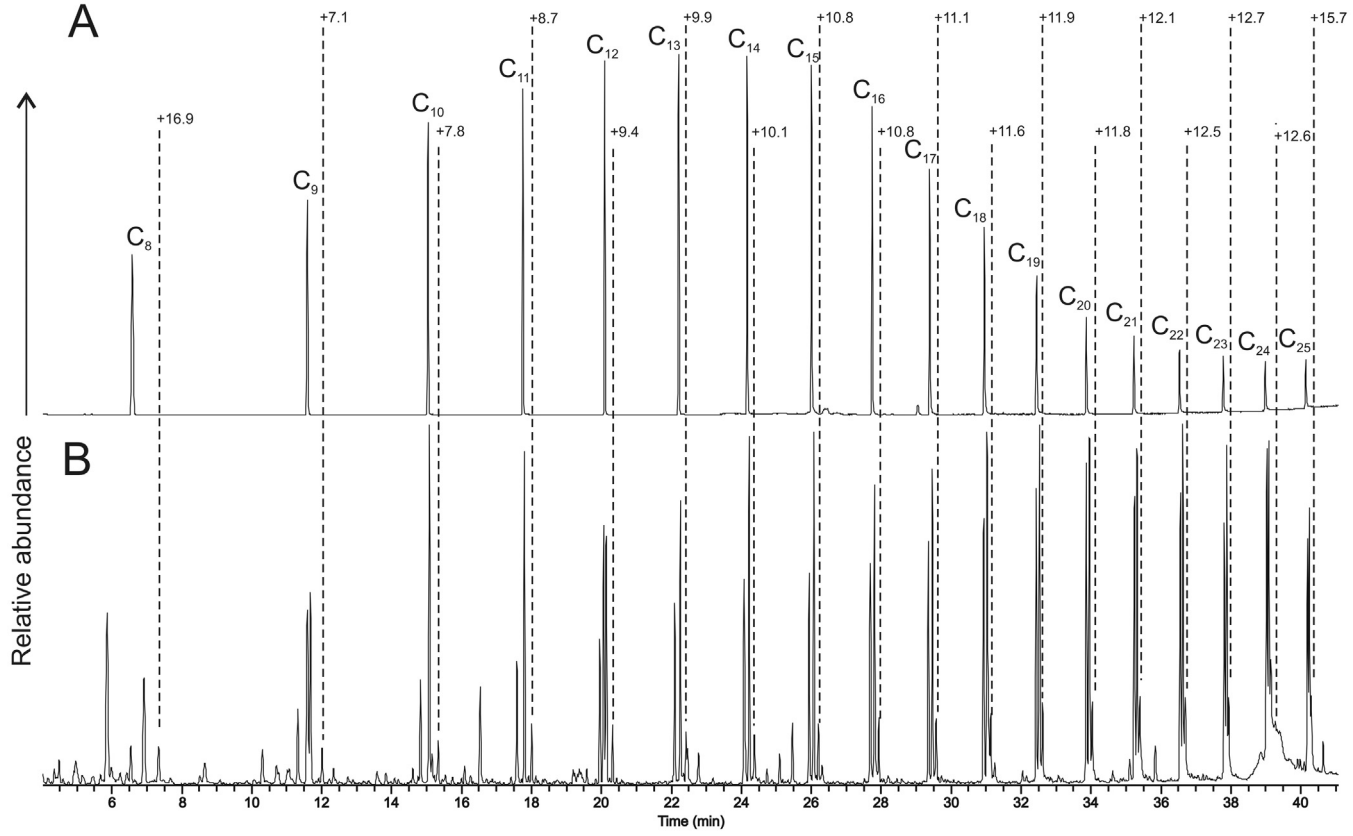

Fig. 1. Partial total ion current chromatogram (A) and pyrogram (B) showing the characteristics of linear alkanes solution and pyrolysis products of polyethylene during GC–MS and Py-GC–MS analysis, respectively. The dotted line indicates the positive difference in linear alkane Kováts RI during Py-GC–MS when calibrated using the linear alkanes solution in the GC–MS analysis.

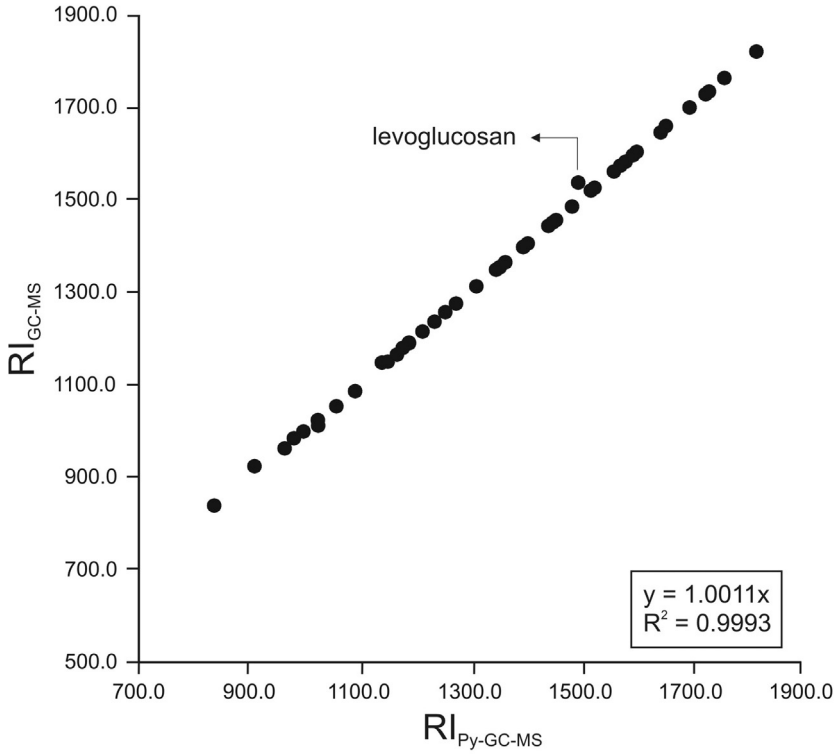

Fig. 2. Comparison of the correlation of the Kováts RI using an equivalent 5%-phenyl-95%-dimethylpolysiloxane stationary phase in the GC–MS and Py-GC–MS systems.