Alkylphenol retention indices

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Abstract

A novel type of retention indices for alkylphenols and related compounds are proposed. The alkylphenol retention indices (APRI) use *para*-substituted *n*-alkylphenols as reference series. APRI for *para-n*-alkylphenols are per definition equal to the number of carbon atoms in the alkyl substituent; the value for phenol is zero. Application of the APRI system with different types of derivatisation of the phenolic hydroxy group showed that the derivatisation has limited influence on these indices. Especially *para*-substituted alkylphenols gave APRI values that could be transferred with high accuracy from one type of derivative to another. By comparing results obtained with different gradients in temperature-programmed GC, it was also shown that APRI is less affected by chromatographic conditions than retention indices based on *n*-alkanes.
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1. Introduction

Alkylphenols, and especially long-chained branched *para*-substituted isomers, are known to have oestrogenic activity and therefore represent an environmental problem. There are several sources of alkylphenols in the environment. Because of the antioxidant properties nonylphenols are used as plastic additives. Nonylphenol ethoxylates are applied as surfactants and emulsifying agents in a large range of industrial products [1,2]. Alkylphenols are present in raw oil and those of shorter alkyl chain may enter the environment via produced water from offshore oil installations [3]. Produced water is defined as the water that comes up with oil and gas from sea bed reservoirs, separated on the platform from the oil and discharged into the sea. The alkylphenols in produced water show an extreme diversity in molecular structure, both with respect to the alkyl substituent and the position of the substituents in the phenyl ring, and several hundred alkylphenols may be present in produced water.

The many isomers represent a challenge in chromatographic analysis of produced water, and accurate characterisation of the chromatographic properties of the compounds would facilitate identification. It is well known that retention indices are more reproducible than retention times, and they are therefore more suitable for characterisation of compounds analysed by gas chromatography. On a retention index scale, the retention of a compound is described in relation to the retention of a series of homologues. The most common system is the Kovats indices [4], where *n*-alkanes are applied as reference compounds. At isothermal conditions there is a linear relationship between $\log t'_R$ and the number of carbon atoms in homologous series, and the Kovats index, I, for a compound, x, can be calculated by the following equation:

$$I_x = 100n \frac{\log t'_{R(x)} - \log t'_{R(z)}}{\log t'_{R(z+n)} - \log t'_{R(z)}} + 100z \tag{1}$$

where t'_R is adjusted retention times of the compound of interest and two *n*-alkanes eluting on each side of the compound. z represents the number of carbon atoms in the *n*-alkane eluting before x, and n is the difference in carbon atoms between the two *n*-alkane references. For maximal accuracy, it is recommended that n is one. Kovats indices acquired at isothermal conditions are usually assumed to be invariant to differences in column dimensions and carrier gas flow, but are highly dependent on the stationary phase and also influenced by the oven temperature. Thus, I acquired at a certain stationary phase at a certain temperature is a characteristic property for a compound that can

be used for identification purposes. In many practical situations, the effect of temperature is small enough to be neglected.

The use of retention indices has been extended to temperature-programmed gas chromatography where there exists an approximately linear relationship between retention times and the number of carbon atoms in a homologous series. In temperature-programmed GC, I is usually calculated by the Van den Dool and Kratz equation [5]:

$$I_x = 100n \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+n)} - t_{R(z)}} + 100z \qquad (2)$$

The parameters n, x and z are the same as in Eq. (1). Eq. (2) gives the same results whether applied with neat retention times or adjusted retention times. As for Eq. (1), it is recommended that n is one. In addition to application of the equations above, various approaches based on higher order regressions have also been applied [6–10].

Although isothermal retention indices are independent of carrier gas flow, column dimensions and phase ratios, temperature-programmed indices are not. All these factors will influence the elution temperature of a compound; increasing the temperature gradient, column length or phase ratio, or decreased carrier gas flow rate, will move the I in the same direction as increased temperature in isothermal chromatography. Thus, I acquired under temperature-programmed conditions are generally less reproducible than I acquired under isothermal conditions [11].

While Kovats indices are the dominating general-purpose retention index system, a large number of alternative series with other calibration compounds than n-alkanes have been applied for special purposes, the most successful approach may be the use of equivalent chain lengths [12] for fatty acid analysis. Alternative retention indices for various purposes have been extensively reviewed elsewhere [13,14]. The motivation for using other calibration standards than alkanes are basically the following:

(1) n-Alkanes cannot be analysed by several common detection methods such as negative ion chemical ionisation mass spectrometry, electron capture detectors and element specific detectors.
(2) Retention indices based on molecules with the same functional groups as the analytes of interest are usually more reproducible, and vary less with chromatographic conditions than I.
(3) A second calibration standard of n-alkanes is not necessary if the retention index scale is defined by some of the analytes of interest.
(4) n-Alkanes have poor chromatographic properties on highly polar stationary phases.

Point 4 is not an issue in alkylphenol analysis, since phases with low to medium polarity are usually preferred. However, the other arguments, especially 1 and 2, are of importance. We therefore propose an alkylphenol retention index (APRI) system based on the homologous series of the *para*-substituted n-alkylphenols. The index for a *para*-substituted n-alkylphenol is by definition equal to the number of carbon atoms in the alkyl substituent. Thus, by the principle devised by Van den Dool and Kratz [5], APRI can be calculated by the following equation:

$$\text{APRI}_x = n \frac{t_{R(x)} - t_{R(z)}}{t_{R(z+n)} - t_{R(z)}} + z \qquad (3)$$

where t_R is retention time of the compound of interest, x, and two *para*-substituted n-alkylphenols eluting on each side of the compound. z represents the number of carbon atoms in the alkyl chains of the *para*-alkylphenols eluting before x, and n is the difference in the number of carbon atoms between the two references. z is zero if the first reference compound is phenol.

It is shown that APRI is more robust than I towards changes in chromatographic properties (temperature gradient) and that APRI to a certain degree can be transferred between different derivatives of the hydroxyl group that is common in alkylphenol analyses. The proposed system is currently applied for characterisation of alkylphenols in water produced from offshore oil installations in the North Sea.

2. Experimental

2.1. Reference compounds

4-(1,1-Dimethylbutyl)phenol; 4-(1-methyl-2,2-dimethylpropyl)phenol and 4-(1,1-dimethylpentyl)phenol were synthesized from the corresponding tertiary alcohols as described elsewhere [15]. Crystalline products were recrystallised from hexane–dichloromethane 3:1 mixture and hexane several times. Liquid products were separated from solvents by rotavapour. The structures and purity of the synthesized products were confirmed by 400 MHz H^1 NMR and GC–MS. Technical nonylphenol was acquired from Sigma–Aldrich (Oslo, Norway). Nonylphenol isomers were identified from the gas chromatographic elution patterns and identifications in [2,16,17]. Other alkylphenols were pure (>97%) reference compounds purchased from Sigma–Aldrich. An n-alkane reference mixture containing every n-alkane from C11 to C26 (except C16) was applied for calculation of I. The n-alkanes were acquired from Kebo-Lab (Oslo, Norway)

2.2. Derivatisations

The phenol hydroxy group was derivatised using three different derivatisation methods. Formate esters of the alkylphenols were prepared by derivatisation with methyl chloroformate (MCF) as described by Grahl-Nielsen [18]. Pentafluorobenzyl ethers were prepared by derivatisation with pentafluorobenzyl bromide (PFBB) as described by Nakamura et al. [19]. Pentafluorobenzoyl esters were prepared from pentafluorobenzoyl chloride (PFBC) according to Boitsov et al. [3]. The structure of the different derivatives can be seen in Fig. 1.

2.3. Gas chromatography

All analyses were performed on an Agilent 6890 GC system connected to an Agilent 5973 mass selective detector with electron impact ionization, and scanning from m/z 50 to 500. A