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## **Aromatic ring-type analysis of complex hydrocarbon mixtures by high-performance liquid chromatography with photodiode-array detection and curve resolution**

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### ABSTRACT

For the resolution of overlapping peaks of high-boiling mineral oil distillates, Meister's method of curve resolution was applied to spectro-chromatograms recorded by means of a high-performance liquid chromatograph coupled to a photodiode-array detector. The algorithm is based on maximizing the dissimilarity between the spectra of the components. The method is universally applicable without a prior knowledge of the spectra and presupposes no limitations concerning the number of components and the shape of their elution profiles. The resolved spectra allow the spectral identification of the aromatic ring types. In addition, the corresponding elution profiles of the compound types can be evaluated, which permits, in principle, quantification of the aromatic ring types.

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### INTRODUCTION

The analysis of mineral oils, their distillation fractions and refinery products is a challenging task because of the very complex composition of the samples. Mineral oils contain aliphatic, alicyclic and aromatic hydrocarbons [1]. Because of the large number of different species, analysis of compound types is more appropriate than analysis of the individual compounds. In this work, hydrocarbons with different aromatic ring numbers were studied, *i.e.*, monoaromatics (benzenes), diaromatics (mainly naphthalenes) and triaromatics (phenanthrenes and anthracenes). Each of these aromatic ring types consists of a large number of individual compounds with normal-, iso- and cyclo-alkyl substituents that differ in number, length and position in the molecule.

Separation of the different aromatic ring types is feasible by using classical liquid chromatography with step-gradient elution [2–5]. However, as these methods

are very time consuming, they are mainly applied on a preparative scale for calibration purposes.

High-performance liquid chromatography (HPLC) enables polycyclic aromatic hydrocarbons to be separated much faster. Chemically modified silica gels are used, with amino, nitro, cyano or aryl substituents as functional groups [6–12]. Although low-boiling petroleum distillates can be separated according to their aromatic ring types, the separation of high-boiling oils, the aromatics of which are much more highly alkylated, is incomplete in HPLC. The resulting peak clusters do not allow precise quantitative analyses. This is a problem of selectivity rather than efficiency; at present there is no chromatographic system of ideal compound-type selectivity available, *i.e.*, high selectivity for different aromatic types and very low selectivity for the numerous alkyl and naphthyl derivatives of a particular type.

The possibilities for the separation of fused peaks can be enhanced by monitoring the chromatogram with several channels; an array detector offers a new dimension in selectivity. In this work, a photodiode-array detector was coupled to the HPLC column, with curve resolution based on a method proposed by Meister for estimating the spectra of the pure components from the spectra of their mixtures [13].

#### THEORY

For linear combinations of spectra in a multi-component mixture, the Lambert–Beer law can be written as

$$\mathbf{a} = \mathbf{B}\mathbf{c} \quad (1)$$

where  $\mathbf{a}$  is a row vector of absorbances at  $m$  wavelengths (the spectrum),  $\mathbf{c}$  is a column vector of concentrations for  $n$  components and  $\mathbf{B}$  is the  $m \times n$  matrix of the absorptivities. By using a photodiode-array detector spectra are recorded along the elution axis at discrete time intervals. From this a family of spectra is obtained at  $l$  times which can be written as an  $m \times l$  matrix of absorbances  $\mathbf{A}$  according to

$$\mathbf{A} = \mathbf{B}\mathbf{C} \quad (2)$$

The matrix  $\mathbf{C}$  consists of  $l$  columns with concentrations of the  $n$  components each. If the absorptivities are known, the concentrations can be calculated from eqn. 2 after rearrangement [14]. If the absorptivities of the components are unknown, principal components analysis (PCA) can be applied to evaluate both the elution profiles and spectra from the data of a spectro-chromatogram.

However, PCA does not give immediately unique solutions for these profiles but results only in vectors which are linear combinations of the real profiles. This means in geometrical terms that the PCA gives the hyperface spanned by vectors corresponding to the real profiles. This ambiguity can be limited by two conditions [15]: (i) only positive values are allowed for the component spectra; and (ii) the concentrations of components are always positive. Hence the range of possible solutions is greatly restricted but not yet unique. Therefore, a third condition was applied in order to obtain a unique solution: (iii) the real profiles should be maximally dissimilar [13]. This condition can be met in the following way. Considering the profiles as

vectors, they are the edges of a hyperpyramid. These edge vectors have to be varied within the first conditions to obtain the hyperpyramid with the greatest possible volume. In practice this is done by changing the edge vectors using non-linear programming until a further increase of volume is impossible.

Other curve-resolution methods are known that are also based on non-negative concentrations and spectra of the components [14,16–22]. As an additional assumption, Osten and Kowalski [16] limited the number of components to two. Lacey [17] and Meader [18] defined a time window that enables three components to be resolved. Resolution of more than three components is feasible by the assumption that every component produces only one maximum [21], by modelling the elution profiles with a Gaussian function [22] or by use of iterative target transformation factor analysis, where possible elution profiles are taken as targets for relating the abstract factors to these profiles [19–21].

Unfortunately, the mentioned additional assumptions are not valid in the present application of resolving complex aromatic mixtures. The elution profiles of the compound types that contain many individual components are far from being Gaussian-like; there may exist several maxima in the elution profiles, and also more than three components (compound types) are possible. Therefore, the application of Meister's method [13] based on the dissimilarity of the spectra and elution profiles can be considered to be the method of choice, and has been applied here to chromatographic data for the first time [23].

## EXPERIMENTAL

HPLC experiments were performed with a Hewlett-Packard 1090A liquid chromatograph. Separation of aromatic ring types was carried out with a column of spherical aminopropylsilica ( $100 \times 2.1$  mm I.D. Hypersil APS,  $5 \mu\text{m}$ ; Hewlett-Packard) with *n*-hexane (for UV spectrophotometry grade; PCK Schwedt, G.D.R.) as eluent, at a flow-rate of 0.3 ml/min. A vacuum gas oil in the boiling range 340–550°C was investigated. The injection volume of  $10 \mu\text{l}$  contained  $5.84 \mu\text{g}$  of the sample dissolved in *n*-hexane.

The spectra were measured in the range 190–308 nm at intervals of 2 nm every 3.7 s and stored on floppy disk. From these data a matrix consisting of 60 wavelengths and 40 elution times was derived for curve resolution with Meister's method [13].

The fractions of mono-, di- and triaromatics were obtained by preparative liquid chromatography according to the API-60 method [2–5] as described elsewhere [23].

## RESULTS AND DISCUSSION

Fig. 1 shows the measured spectro-chromatogram demonstrating the overlapping peaks of monoaromatics (maximum at about 1.5 min) and diaromatics (maximum at 1.9 min). The triaromatics can be barely recognized at a retention time of about 3 min.

Application of the curve-resolution method to the spectro-chromatogram gives a large number of eigenvalues that is only limited by the dimensionality of the second-

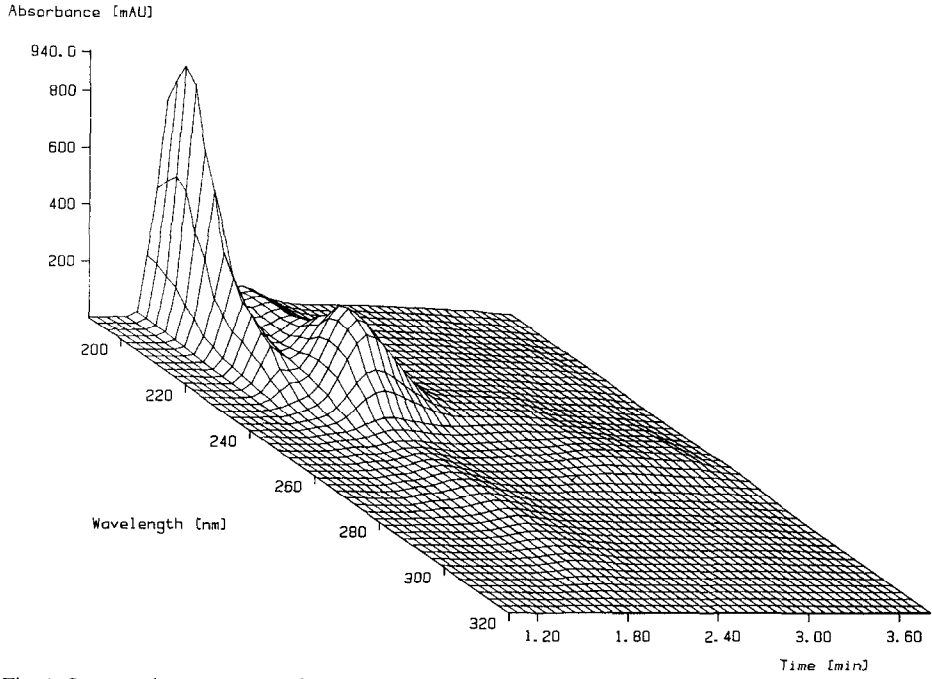


Fig. 1. Spectro-chromatogram of a vacuum gas oil (boiling range 340–550°C)

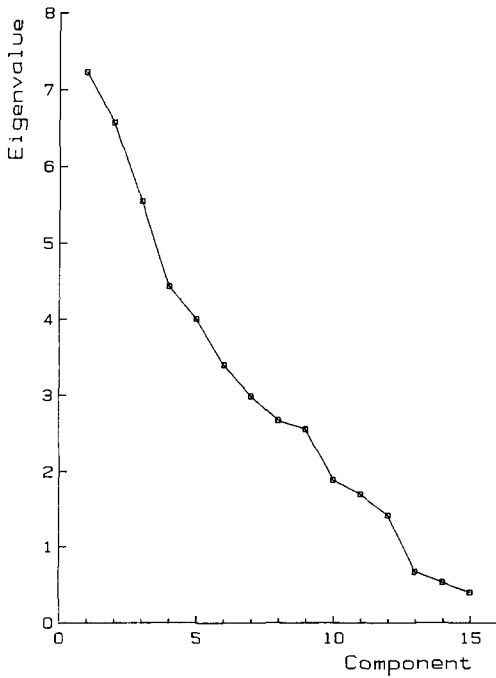


Fig. 2. Variation of the logarithms of eigenvalues for the initial fifteen principal components of the vacuum gas oil (see Fig. 1)

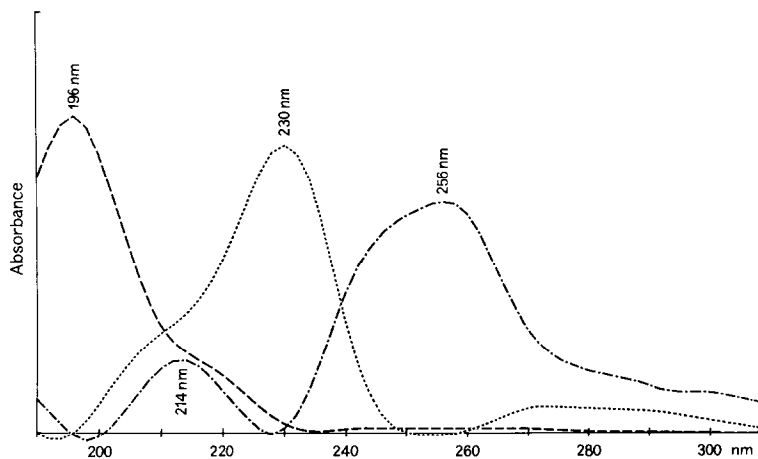


Fig. 3. Resolved spectra for three components: --- = monoaromatics; ... = diaromatics; — · — = triaromatics.

moment matrix, *i.e.*, 40 eigenvalues can be computed. In Fig. 2, the logarithms of the eigenvalues for the initial fifteen principal components are plotted. These eigenvalues represent different spectral components under the spectro-chromatogram. Hence it is confirmed that not only a few types are obtained but also several groupings of individuals exist under the spectro-chromatogram. As also seen in Fig. 2, there is no definite jump in the dependence of the eigenvalues on the number of components, which would indicate a boundary between existing components and structured noise. For this reason, in the present instance the number of relevant components (compound types) has to be fixed by the experimenter. Basically, this is possible because the principal components are obtained in decreasing order of importance for explain-

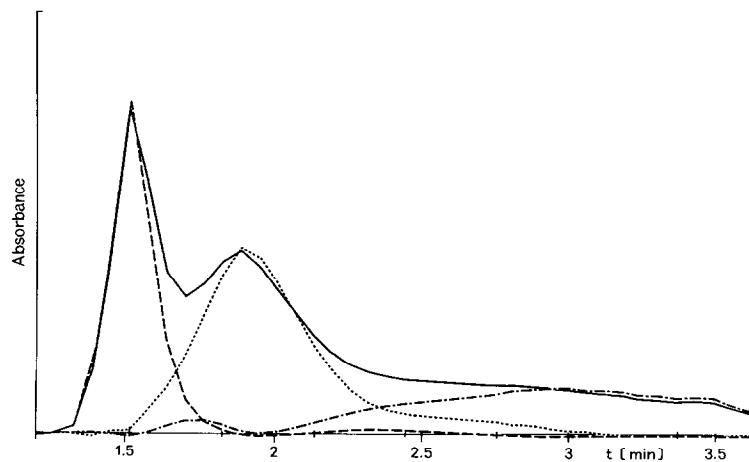


Fig. 4. Resolved elution profiles for three components in the chromatogram measured at 210 nm; --- = monoaromatics; ... = diaromatics; — · — = triaromatics.

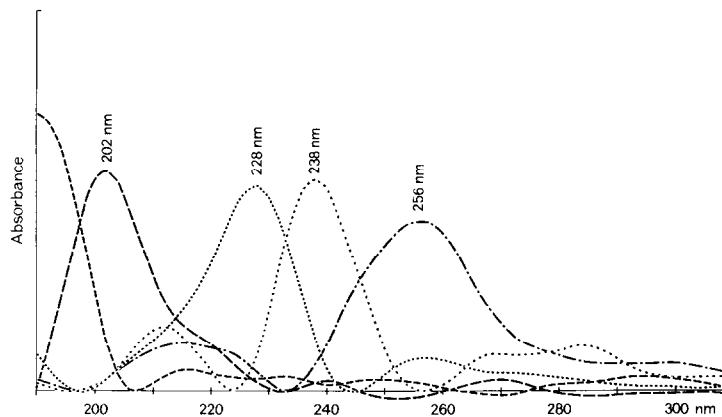


Fig. 5. Resolved spectra for five components.

ing the variance in the data: therefore, the highest eigenvalues, here the initial principal components, represent the most important compound types.

The results of curve resolution for assuming three principal components give spectra (Fig. 3) in which the shape and maxima correspond to those obtained by preparative liquid chromatography [23]. Of course, no information about the absolute absorbance value can be derived as long as the absorptivities are unknown. In Fig. 4, the corresponding elution profiles are given, obtained by relating the abstract elution profiles to a chromatogram recorded at 210 nm in such a way that the individual elution profiles add to give the measured chromatogram. In this way, quantitative analysis would be possible by integration over the elution profiles multiplied by previously determined calibration factors.

In addition to the assumptions of three relevant principal components, also component numbers 2, 4 and 5 were tested. For  $n = 2$  the spectra and the elution profiles of di- and triaromatics overlap. With  $n = 4$  the monoaromatics and for  $n = 5$

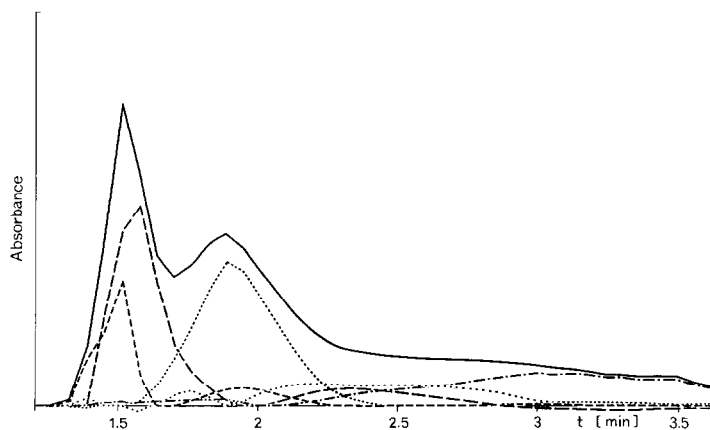


Fig. 6. Resolved elution profiles for five components in the chromatogram measured at 210 nm.

also the diaromatics split into two components each. Figs. 5 and 6 demonstrate the results of curve resolution for five principal components. The example shows that by increasing the number of principal components other spectral components could be found. However, these components are irrelevant for characterizing the compound types in the present instance.

For the tested vacuum gas oil, the final number of relevant components was fixed at three because the resulting spectra (Fig. 3) are in agreement with the previously determined spectra of the isolated fractions.

## CONCLUSION

Overlapping peaks of complex hydrocarbon mixtures can be resolved by the curve-resolution method used [13] into several principal components representing spectra and elution profiles. However, the number of principal components (relevant compound types) cannot be derived from the algorithm because no distinct cut is observed between experimental error and physically meaningful components. If the spectra of the components are known, as in the present instance owing to preparatively obtained fractions of the compound types, the number of relevant components can be fixed by the analyst.

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