Reviews

Optimization of Gas Chromatographic Analytical Methods for Toxic Compounds in Air*

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This is a review article concerning the development of a gas chromatographic analytical method for the analysis of 70 air toxic compounds. Not only the operating conditions, but also the column system is optimized. Optimization of the GC analytical methods for air toxic compounds is based on a unified method with a system comprising two columns. An optimization strategy with stepwise temperature programming has been used to achieve optimum separations. Two sets of usual GC instruments with specially developed software, Chromatogram Analyzer, have also been used for this purpose. Some essential retention data and typical results are presented in this paper.

Keywords Gas chromatography, analytical method, optimization, air toxic compound

1 Introduction

Developing and optimizing gas chromatographic analytical methods for environmental pollutants have become very important in recent years. In order to monitor the ozone precursors and to control the emission of pollutants in air, 190 air toxic compounds have been specified by the United States in the Amendment of Clean Air Act of 1990. In cooperation with the U.S. EPA, 70 toxic compounds were investigated in our laboratory for this purpose. The GC Expert System developed by us has been used to develop and optimize GC analytical methods for these toxic compounds. This article provides only a review of this research work.

2 Method Optimization

As indicated in our expert system, one of the most important points in the optimization of GC analytical methods is that optimization must include not only optimization of the operating condition, but also recommendations concerning an optimum column system; the optimum operating condition does not involve linear programming, but stepwise temperature programming.

2.1 Column recommendation

Method development actually begins with column selection. Since most of the air toxic compounds listed in Table 1 are organic, and volatile compounds, they can be analyzed by gas chromatography. Also, according to the method reported in our previous paper, compounds with different molecular formulae or having different functional groups are easily separated using high-resolution gas chromatography with either nonpolar or small polar columns. Meanwhile, there is no special isomer, such as an enantiomer, involved in developing an analytical method.

Currently, the separation of these compounds usually uses 6 to 7 columns involving different EPA's methods. This is not only due to the difficulty in separating hundreds of target toxic compounds, but also due to the difficulty in separating from the matrix components. Therefore, new methods and new columns are continuously being developed in order to overcome these difficulties. However, since each method is developed for the separation of a special group compounds or for different matrices, the method is only suitable for a special case. Although some different analytical methods have the same target components, the analysis results

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Table 1 Coefficients of A and B in the gas chromatographic retention equation of the same compounds are different. In order to solve the separation problems and to eliminate any contradictions, a unified method comprising a system of two columns has been developed by us using our expert system. Since most of the analytes are polar compounds, according to the rules of column selection reported in our previous paper, the most suitable column is with a nonpolar or slightly polar stationary phase. Since these compounds are different in molecular structure or polarity, a system of two columns with a slight polarity difference is sufficient for performing both the separation and supplementary separations for these components. A system comprising two columns with a large polarity difference is only suitable for the separation of complex mixtures which contain homologues and special isomers. For a polar phase, such as Carbowax 20M, the separation range of the temperature is limited; this means that for some very volatile compounds the retention values (capacity factor $k'$) on such a column are too low, i.e. either $k'<0.2$ or $k'>20$. Therefore, in order to separate the components listed in Table 1 it is unnecessary to select columns having a great difference in polarity.

Based on comparisons of both the theoretical and experimental retention data, a DB-1 column and a DB-1301 column were finally chosen as the optimum column system for developing an analytical method for these toxic compounds in air.

### Optimization of the operating conditions

Toxic organics with different functional groups usually have different elution orders on different columns, even at different temperatures. The reason for this seems to be simple. Compounds with different functional groups, structures and polarities have different van der Waals interactions with the stationary phase. Therefore, optimization of separation for these compounds using temperature programming can cause many elution order changes, as shown in Fig. 1. In order to avoid the crossing point for a crossover pair,
the ramp rate is usually changed. However, for a very complicated mixture it is impossible to avoid hundreds of crossing points and to achieve optimum separation by using only linear programming. Therefore, an intelligent optimization strategy is used in the optimization of separation involving a stepwise temperature gradient. The strategy mainly contains three steps:

1) Obtain an overlapping separation range mapping (OSRM), as indicated in Fig. 2, from the basic retention data listed in Table 1, as shown in Fig. 1. This means that the resolution ($R_s$) for any pair given in Fig. 1 can be calculated by using our Expert System software. If $R_s < 1.5$, solid lines are drawn as indicated in Fig. 2; if $R_s = 0$, a ring is also drawn for the crossing point of a given pair at the given temperature. In this way, an OSR mapping for all of the components in a sample can be obtained as described in our previously published work.

Fig. 1 Plot of the retention value ($\ln k'$) vs. the inverse absolute temperature ($1/T$) for the sample containing 55 toxic organics on a DB-1 column (J&W Scientific Inc.) with 60 m x 0.25 mm i.d., film thickness 0.25 µm. The range of the capacity factor ($k'$) is from 0.2 to 20 and the range of the temperature is from 0°C to 220°C.

Fig. 2 Overlapping separation range mapping of the 55 components on DB-1 column. The solid line indicates the unseparable range of the temperature ($R_s < 1.5$) for a corresponding solute; the ring indicates the crossing point of the solute with its neighbor. The initial stages of the temperature in separating these components can be obtained as indicated by the horizontal lines, which means components 1 to 6 should be eluted at 38°C in the first stage, and components 7 to 33 should be eluted at 43°C in the second stage; the left stages are at 133, 150 and 224°C, respectively, for the remaining components.

Fig. 3 Eluted profile of the first group compounds at the optimum temperature gradient. The instrument is a Model 1003 GC equipped with an FID detector at 250°C, and split injection (1:130) at 240°C. The column is the same as that described in Fig. 2. The operating condition is: initial temperature 30°C for 4 min; heat to 43°C at 30°C/min; keep at 43°C for 21 min; ramp to 125°C at 30°C/min; hold for 4 min, then heat to 220°C at 30°C/min and keep for 10 min. The peak identities are listed in Table 2.

Fig. 4 Chromatogram analyzed result by the software. The upper chromatogram is the actual eluted profile; the middle was simulated by the software; and the last is the subtracted one, which contains information concerning the unresolved peaks, as listed in Table 2.
Based on the OSR mapping, the initial schedule of the temperature gradients can be inferred.

2) Correct the temperature stage by a computer simulation of solute migration in the column after considering the solute concentration; also, achieve a desirable separation for the least-separable pair on the current stage.

3) Revise the later temperature gradients after taking into account the current position of each solute in the column. Also, if necessary, a series of OSR mappings can be obtained in order to revise the temperature schedule. Repeat steps 2) and 3) until the last component has been eluted.

In principle, 70 toxic compounds can be analyzed simultaneously; however, concerning the possibility of chemical reactions among toxic compounds, they are divided into two groups. One contains 55 neutral and acid compounds; the other group contains 15 neutral base compounds.

An optimized separating condition with 4 stages of temperature gradient has been obtained on a nonpolar column (DB-1) for the 55-component sample. The actual chromatogram is as in Fig. 3. Meanwhile, an optimum separating condition with 3 stages of the temperature gradients has been achieved on a slightly polar column (DB-1301) for the same sample. The 5 pairs of unseparable components on the DB-1 column can be separated by the DB-1301 column, and 2 pairs on the DB-1301 column can be separated by the DB-1 column in reverse.

### Chromatogram Analyzer

A multi-dimensional GC system is a well-known system. For separating complicated mixtures, although a system having two columns is required (as discussed above), operating an actual multi-dimensional column system with a column switching system is not very easy. It is more convenient to use only two ordinary sets of GC instruments with a column difference from one another as well as a Chromatogram Analyzer that we have developed. A software of chromatogram analyzer performs analyses of the peak purity and resolution of overlapping peaks in order to obtain accurate results concerning quantitation and identification for overlapping and matrix interfering peaks.

The Chromatogram Analyzer is based on an exponential modified Gaussian (EMG) function. The parameters in the EMG function are obtained in isothermal elution by using a retention time-dependence linear relationship and are extended to temperature-gradient elutions. Further, it is necessary to correct the peak area, retention time and linear relation in order to obtain a chromatogram with the correct subtracted
result\textsuperscript{24}, as shown in Fig. 4. The peak identities of Fig. 4 are listed in Table 2.

4 Conclusions

It has been proven that the GC Expert System is an effective means in developing and optimizing GC analytical methods for environmental samples. Also, because the method optimization is based on a unified method and the Chromatogram Analyzer is used to resolve overlapping peaks, a large variety of samples having different compositions and different matrices can be analyzed by such a unified method.

References


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