

Gas chromatographic separation and determination of chloroanthracene isomers on fly ash

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Abstract—An efficient, reproducible and rapid fused silica capillary column gas chromatographic method, in splitless mode, for analysing of the three chloroanthracene isomers is described. The method affords efficient separation and good linearity for each isomer in the range of 0.2–200 µg/ml. The method can also be used in separation and determination of another thirty three aromatic and their halosubstituted compounds. This paper also presents the applications of the method in analysing of complex products mixture from reaction of the selected aromatic compounds with hydrogen chloride on fly ash surface from municipal incinerator.

Keywords: gas chromatography; chloroanthracene isomers; fly ash.

INTRODUCTION

Isomers of chloroanthracene (CA) are important industrial organic intermediates and find extensive use in the manufacture of plastic, rubber chemicals and drugs. Also, they are extremely toxic and find their way into effluents.

A survey of literature released some instrumental analytical methods for the direct measurement of CA isomers (Campbell, 1984; 1982; Bright, 1985; Imasaka, 1987). Campbell and Grimsrud (1984; 1982) proposed using gas chromatography (ECD) based on comparison of response coefficient variation in measuring unseparate isomers before or after the addition of trace oxygen to GC carrier gas. Bright *et al.* (1985) developed a new phase resolution fluorescence method that could determine CA isomers and Imasaka *et al.* (1987) proposed high performance liquid chromatography (HPLC) with supersonic jet/laser fluorometric detection to analyze isomers involving three CA isomers. All these techniques proposed took chloroanthracene isomers as representative to demonstrate that methods are feasible. No gas chromatographic method has, however, been reported describing analytical quantitation of three CA isomers separated individually. It would be extremely desirable to develop a faster, cheaper and simpler technique for determination of the three CA isomers by GC.

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Since fused silica capillary column gas chromatograph is easy to work in combination with mass spectrometer for identification of products mixture, this paper is describing a fused silica capillary column gas chromatographic method for determination of CA positional isomers from fly ash surfaces of municipal incinerator by direct gas chromatography and gas chromatograph-mass spectrometric method (GC-MS) after extraction. The method proposed here is rapid and simple for accurate estimation not only for the three isomers of CA, but also for another 33 selected aromatic and mono-, di/bi- and tricyclic halogen- substituted aromatic compounds such as toluene, chlorobenzene, chlorotoluene isomers, mesitylene, bromobenzene, anisole, benzyl chloride, chlorobromobenzene isomers, methylbenzoate, naphthalene, chloronaphthalene isomers, nitrobenzene, chloronitrobenzene isomers, biphenyl, chlorobiphenyl isomers, dibiphenyl ether, acenaphthylene, diphenyl methane, anthracene, chloroanthracene isomers, dichloroanthracene and so on.

EXPERIMENTAL

Apparatus

A HP 5890 gas chromatograph from Hewlett-Packard Corp. USA equipped with flame ionization detector. Helium carrier gas and splitless injection were used.

Materials

Bonded fused silica capillary columns: RSL-150, RSL-200, RSL-300, RSL-400, RSL-500 and Super OX II was supplied by Applied Science Inc.. Isomers of CA: 1-CA, 2-CA, 9-CA, and other reference samples used in this work were produced by Aldrich Inc.. All solvents used were GC-MS grade.

RESULTS AND DISCUSSION

1-chloroanthracene (1-CA) and 9-chloroanthracene (9-CA) are the most difficult-separated-pair among the three CA isomers: 1-, 2-, and 9-chloroanthracene (9-CA) in gas chromatography. They can not be successfully separated by conventional capillary columns such as SE-30, SE-54, OV-17, OV-101, DB-5 and so on, which has usually been used in the separation of many other organic chlorides and/or polycyclic aromatic compounds. It is obvious that the separation of 1- and 9-CA can not be achieved in relatively low polarity column. We have systematically examined RSL-150, RSL-200, RSL-300, RSL-400 fused silica capillary columns for the separation efficiency of these three CA isomers. Although 25-30 meter long columns were chosen and low column temperature programming rate was used (from 50 °C and then up to 210 °C at 2 °C /min.), we still did not get the desired results (Fig. 1a).

With RSL-500 fused silica capillary column, the separation efficiency of 1-CA and 9-CA was rather improved and resolution of $R=0.2$ was achieved. However, 9-CA still could not be

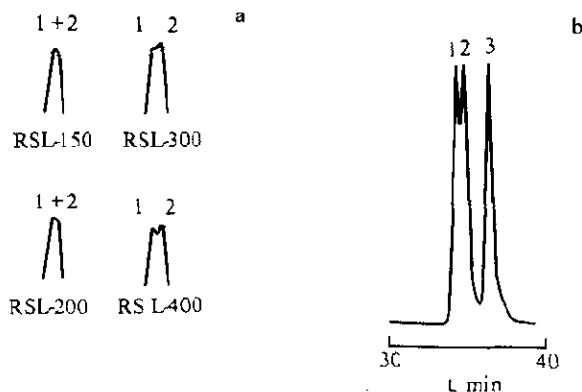


Fig. 1 Chromatographic separation of chloroanthracene isomers

Column temperature from 50 °C to 210 °C at 2 °C /min, helium carrier gas, flame ionization detector, and bonded fused silica capillary column: (a) RSL-150, 30m; RSL-200, 15m; RSL-300, 30m; and RSL-400, 15m (b) RSL-500, 25m
1. 9-chloroanthracene 2. 1-chloroanthracene 3. 2-chloroanthracene

completely separated from 1-CA (Fig. 1b). The eluant order for RSL-500 column, like other RSL columns above, was as follows: first, 9-CA, 1-CA and 2-CA. This is easy to understand by structures of both anthracene and chloroanthracene isomers. It is known from anthracene chemistry that abundant electron concentrates on 9-substituted position (anthracene medium-position). Therefore, 9-CA has a higher polarity than 1-CA. And it is clear that 9-CA should appear earlier than 1-CA in the eluation from column. For the similar reason, anthracene in the chromatogram has a shorter retention time than CA isomers, and 9, 10-dichloroanthracene (9,10-DCA), on the contrary, has a much longer retention time (Fig. 2). Although modification of separation method of CA isomers using even lower GC column temperature worked fine, it was however not very much used in practice due to their too long the retention time, and thus leading to low sensitivity and poor quantitative accuracy (Fig. 2).

Further observation released that SuperOX II fused silica capillary column had much better separation for CA isomers (Fig. 3a), which used stationary phase of polyethyleneglycol and has a high polarity. The separation of CA isomers could be completed in 20 minutes. Although a good separation can be obtained isothermally at 180 °C, a even higher column efficiency could be seen with programmed temperature technique (Fig. 3b). The total analysis time is shortened only to 25 minutes. The method affords a good linearity for each isomer in the range of 0.2-200 µg/ml (Fig. 4). Results of the analysis of synthetic mixtures are given in Table 1. Analyses were made by utilizing the internal standard method and are quite efficient as shown by accuracy of the determination to an extent of 2%.

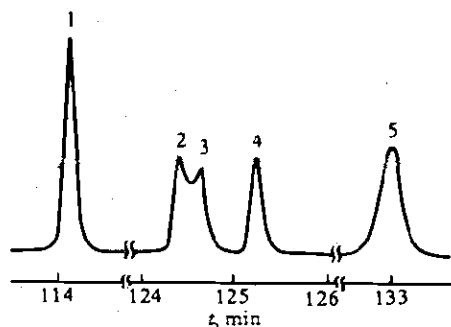


Fig. 2 Chromatographic separation of chloroanthracene isomers RSL-500 (25m) boned fused silica capillary column

Programmed temperature from 20°C to 100°C at 4°C/min, then up to 210°C at 1°C/min. Helium carrier gas, and flame ionization detector.

1. anthracene 2. 9-chloroanthracene 3. 1-chloroanthracene
4. 2-chloroanthracene 5. 9,10-dichloroanthracene

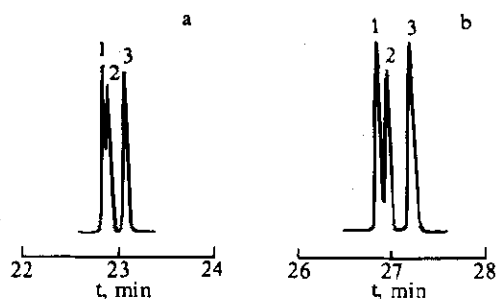


Fig. 3 Chromatographic separation of chloroanthracene isomers

Chromatographic condition: 15m × 0.32mm i.d. SuperOX

II fused silica capillary column coated with

Polyethyleneglycol, Helium carrier gas, Flame

ionization detector. (a) Isothermal column temperature

at 180°C; (b) Column temperature from 50°C to 100°C

at 4°C/min, and final to 210°C at 6°C/min

1. 9-chloroanthracene 2. 1-chloroanthracene 3. 2-chloroanthracene

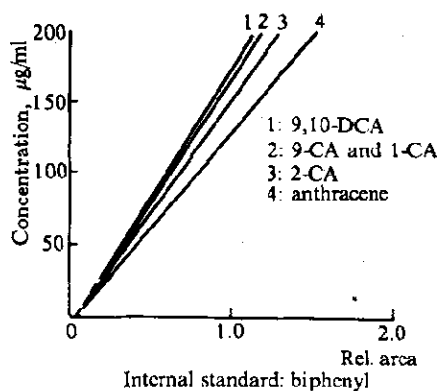


Fig. 4 Calibration curves of anthracene, CA isomers and 9, 10-DCA by SuperOX II fused silica capillary column

Table 1 Analysis of synthetic mixtures

| Amount present | Amount found* | Error, % |
|----------------|---------------|----------|
| 200ng anth. | 196.7 | -1.65 |
| 1-CA | 197.1 | -1.45 |
| 2-CA | 202.8 | +1.40 |
| 9-CA | 203.4 | +1.70 |
| 2µg anth. | 2.04 | +2.0 |
| 1-CA | 1.98 | -1.0 |
| 2-CA | 2.02 | +1.0 |
| 9-CA | 2.01 | +0.5 |
| 20µg anth. | 19.67 | -1.65 |
| 1-CA | 20.12 | +0.60 |
| 2-CA | 20.22 | -1.10 |
| 9-CA | 20.04 | +0.20 |
| 100µg anth. | 99.12 | -0.88 |
| 1-CA | 99.83 | -0.17 |
| 2-CA | 101.1 | +1.10 |
| 9-CA | 100.5 | +0.50 |
| 150µg anth. | 149.1 | -0.60 |
| 1-CA | 150.6 | +0.40 |
| 2-CA | 150.1 | +0.07 |

Table 1 (Continued)

| Amount present | Amount found* | Error, % |
|-------------------|---------------|----------|
| 9-CA | 151.0 | +0.67 |
| 200 μ g anth. | 203.3 | +1.65 |
| 1-CA | 198.6 | -0.70 |
| 2-CA | 203.6 | +1.80 |
| 9-CA | 201.8 | +0.90 |

* Average of 5 determinations anth — anthracene

CA — chloroanthracene

Fig. 5 shows chromatogram of reaction products of anthracene with gaseous hydrogen chloride on fly ash surface from a municipal incinerator, which are consisted of major products of CA, DCA and even more chlorine. They were all separated nicely. Most of large peaks in the chromatogram of the chlorination products on fly ash was attributed to siloxanes. Using a reaction temperature of 150 °C and a volume of 175ml of HCl introduced over a period of 20 minutes, chlorination of anthracene on fly ash (Chicago, Coal, Toronto, Hamilton) gave chlorinated products listed in Table 2. Monochlorinated isomers 1-, 2-, and 9-CA were separated and quantitated by gas chromatography, while the higher chlorinated congeners were analyzed by GC/MS using SIMS for quantitation. The yield in Table 2 is the average of several runs. It is seen that these yields have deviations from the average of about +2.0%. We attribute deviation of this magnitude to heterogeneous nature of fly ash, since errors were encountered and compared in simple recovery experiments in which no chlorination took place (vide infra). Importance of the data are observed in the trends, and more than the errors.

Table 2 Chlorination of anthracene (% yield from 100mg starting material, corrected for recovery)
at 150 °C with 350ml HCl

| Fly ash | Chicago | Coal | Toronto | Hamilton |
|---------------|-----------------|------------------|-----------------|-----------------|
| Anthracene | 0.24 \pm 0.04 | 41.95 \pm 7.88 | 0 | 1.43 \pm 0.27 |
| 1-Cl-anth. | 0.33 \pm 0.06 | 0 | 0 | 0.82 \pm 0.15 |
| 2-Cl-anth. | 0 | 0 | 0 | 0 |
| 9-Cl-anth. | 2.91 \pm 0.28 | 42.07 \pm 4.12 | 0 | 0.55 \pm 0.11 |
| 9,10-Cl-anth. | 18.21 \pm 3.2 | 19.83 \pm 2.38 | 6.73 \pm 1.11 | 1.26 \pm 0.20 |
| Cl-anth. | 4.82 \pm 0.33 | 2.37 \pm 0.41 | 2.23 \pm 0.38 | 0.32 \pm 0.05 |
| Cl-anth. | 1.73 \pm 0.21 | 1.88 \pm 0.33 | 1.13 \pm 0.21 | 0.43 \pm 0.07 |

Results of Table 2 show that fly ash can act as an efficient promoter for aromatics as

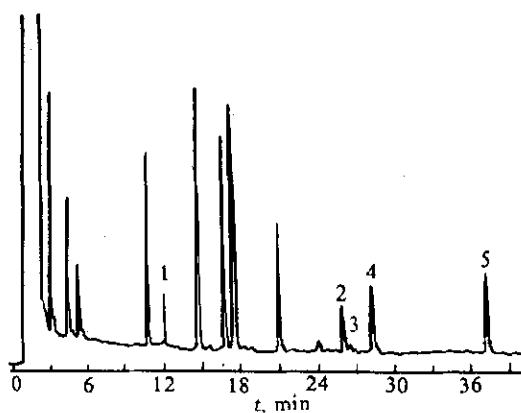


Fig. 5 Chromatogram of products of the reaction of anthracene with gaseous HCl on the fly ash surface from municipal incinerator in Chicago
 Chromatographic condition: 15m \times 0.32mm i. d. SuperOX II fused silica capillary column. Column temperature from 20 $^{\circ}$ C to 50 $^{\circ}$ C at 2 $^{\circ}$ C/min, then to 100 $^{\circ}$ C at 40 $^{\circ}$ C/min, and final to 210 $^{\circ}$ C at 6 $^{\circ}$ C/min. Helium carrier gas. Flame ionization detector
 1. anthracene 2. 9-chloroanthracene 3. 1-chloroanthracene
 4. 2-chloroanthracene 5. 9, 10-dichloroanthracene

much as up to 25-60% of the adsorbed anthracene is converted to halogenated products. We also found that SuperOX II could successfully separate not only 1-, 2-, and 9-CA, but also another 33 aromatic and haloaromatic compounds, involving toluene, chlorobenzene, chlorotoluene isomers, mesitylene, bromobenzene, anisole, benzyl chloride, chlorobromobenzene isomers, methylbenzoate, naphthalene, chloronaphthalene isomers, nitrobenzene, chloronitrobenzene isomers, biphenyl, chlorobiphenyl isomers, dibiphenyl ether, acenaphthylene, diphenyl methane, anthracene, chloroanthracene isomers, and dichloroanthracene and so on. The related retention data are listed in Table 3 and chromatogram of their mixture is shown in Fig. 6. It should be noticed that 1-, and 2- chloronaphthalene can also be separated satisfactorily which is another difficult-separation-pair by capillary gas chromatographic column and 2-CN is one of priority pollutants listed by USEPA, so that several works about development of new liquid crystal stationary phases have been published recently (Chiabari, 1974; Sakagami, 1984). It should also be noticed that the multistep programmed temperature technique was used in Fig. 6, which was very useful for analysis of sample mixture with wide range of boiling points. In that way, the total analytical time could then be shortened to be the shortest without any significant loss of the resolution efficiency of

the compounds. A good sample from municipal incinerator fly ash can be made by using organic solvents of either methylene or hexane/acetone (1:1) to extract before gas chromatography or GC-MS is to be attempted.

Table 3 The retention data of the selected aromatic and their halosubstituted compounds
 Chromatographic condition: 15m \times 0.32mm i. d. SuperOX II fused silica capillary column coated with polyethyleneglycol. Column temperature from 20 $^{\circ}$ C to 50 $^{\circ}$ C at 2 $^{\circ}$ C/min, then to 100 $^{\circ}$ C at 4 $^{\circ}$ C/min, and final to 210 $^{\circ}$ C at 6 $^{\circ}$ C/min.
 Helium carrier gas. Flame ionization detector

| Compounds | R. T. | Rel. R. T. |
|----------------------------|--------|------------|
| 1 Toluene | 4.47' | 0.184 |
| 2 Chlorobenzene | 10.91' | 0.448 |
| 3 Mesitylene | 12.30' | 0.506 |
| 4 2-chlorotoluene | 15.76' | 0.647 |
| 5 3-chlorotoluene | 16.05' | 0.659 |
| 6 Butylbenzene | 16.21' | 0.666 |
| 7 4-chlorotoluene | 16.62' | 0.683 |
| 8 Bromobenzene | 18.30' | 0.753 |
| 9 Anisole | 18.83' | 0.774 |
| 10 Tetradecane | 24.34' | 1.000 |
| 11 Benzyl chloride | 31.59' | 1.298 |
| 12 1-Chloro-3-bromobenzene | 31.66' | 1.301 |
| 13 1-Chloro-4-bromobenzene | 33.51' | 1.376 |
| 14 1-Chloro-2-bromobenzene | 36.53' | 1.501 |
| 15 Methylbenzoate | 36.53' | 1.501 |
| 16 Naphthalene | 42.64' | 1.752 |
| 17 Nitrobenzene | 42.83' | 1.761 |
| 18 1-chloro-3-nitrobenzene | 52.10' | 2.141 |
| 19 1-chloro-4-nitrobenzene | 54.27' | 2.231 |
| 20 Biphenyl | 56.43' | 2.318 |
| 21 2-chloronaphthalene | 57.29' | 2.353 |
| 22 1-Chloronaphthalene | 57.59' | 2.366 |
| 23 1-Chloro-2-nitrobenzene | 57.59' | 2.366 |
| 24 Diphenyl ether | 57.87' | 2.378 |
| 25 2-chlorobiphenyl | 63.89' | 2.625 |
| 26 Acenaphthylene | 65.30' | 2.683 |
| 27 3-Chlorobiphenyl | 69.19' | 2.843 |
| 28 4-chlorobiphenyl | 70.03' | 2.877 |
| 29 Diphenyl methane | 74.76' | 3.071 |
| 30 Tetracosane | 77.36' | 3.178 |
| 31 Anthracene | 86.72' | 3.563 |

Table 3 (Continued)

| Compounds | <i>R. T.</i> | Rel. <i>R. T.</i> |
|-----------------------------|--------------|-------------------|
| 32 Diphenyl chloromethane | 90.71' | 3.727 |
| 33 9-chloro-anthracene | 96.79' | 3.977 |
| 34 1-chloro-anthracene | 97.11' | 3.990 |
| 35 2-chloro-anthracene | 97.90' | 4.022 |
| 36 9, 10-Dichloroanthracene | 103.92' | 4.271 |

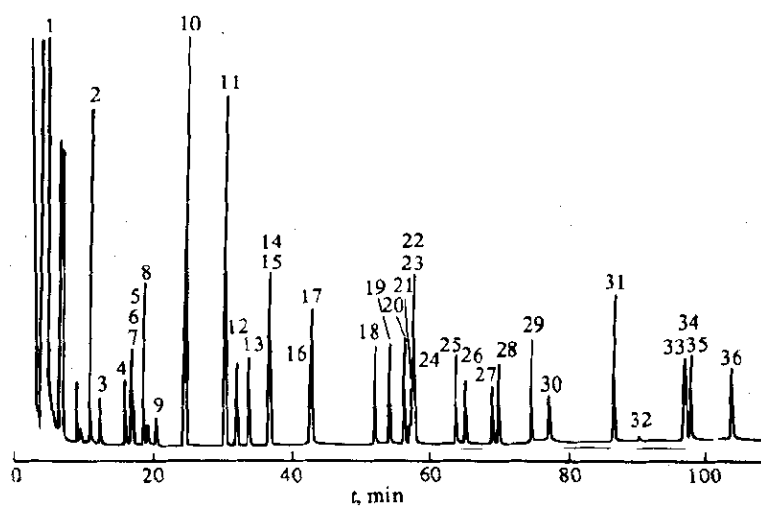


Fig. 6 Chromatogram of the selected aromatic and their halosubstituted compounds
 Chromatographic condition: 15m× 0.32mm i. d. SuperOX II fused silica capillary column coated with polyethyleneglycol. Column temperature from 20 °C to 50 °C at 2 °C/min, then to 100 °C at 4 °C/min, and final to 210 °C at 6 °C/min.
 Helium carrier gas. Flame ionization detector

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