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PERFLUORO AND CHLORO AMIDE DERIVATIVES OF ANILINE AND CHLOROANILINES: THEIR FORMATION AND GAS CHROMATOGRAPHIC DETERMINATION BY MASS SELECTIVE AND ELECTRON-CAPTURE DETECTORS

by
Hing-Biu Lee

Research and Applications Branch
National Water Research Institute
Environment Canada
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario, Canada L7R 4A6

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MANAGEMENT PERSPECTIVE

Many aromatic amines such as aniline and its chlorinated analogs are toxic or carcinogenic. Since these compounds are widely used by chemical industries as starting materials or intermediates of many dyes, pesticides and pharmaceuticals, anilines are often found in the environment as industrial wastes or degradation products of pesticides. However, sensitive and specific analytical methods suitable for the monitoring of aniline and chloroanilines in the environment are still lacking. This paper describes a procedure that is applicable to the trace analysis of substituted analines and numerous other carcinogenic compounds with an amino group.

The study was carried out at the request of the Water Quality Branch and was conducted during 1987/88 as part of the NWRI Analytical Chemistry Research Project.

PERSPECTIVE-GESTION

Bon nombre d'amines aromatiques comme l'aniline et ses dérivés chlorés sont toxiques ou cancérogènes. Comme les anilines sont très employées en chimie industrielle, notamment comme produit de base ou intermédiaire dans la fabrication d'un grand nombre de colorants, de pesticides et de produits pharmaceutiques, on en retrouve souvent dans l'environnement sous forme de rejets industriels ou de produits de décomposition de pesticides. Toutefois, il n'y a encore pas de méthode d'analyse assez sensible et spécifique pour la surveillance de l'aniline et des chloroanilines dans l'environnement. On présente ici une méthode pouvant s'appliquer à l'analyse des anilines substituées et de nombreuses autres amines cancérogènes présentes à l'état de traces.

Cette étude a été commandée par la Direction de la qualité des eaux et réalisée en 1987-88, dans le cadre du Projet de recherche en chimie analytique de l'INRE.

SUMMARY

The preparation of the amide derivatives of aniline and 16 chloroanilines by reaction with trifluoroacetic, pentafluoropropionic, heptafluorobutyric, chloroacetic, and dichloroacetic anhydrides is described. Separation of these derivatives by capillary columns was investigated and mass spectral data of 85 derivatives obtained by a mass selective detector were summarized. Electron-capture relative response factors of the amides were also obtained. A comparison of the five derivatization reactions indicated that the heptafluorobutyryl derivatives were most suitable for the analysis of the present group of anilines.

RÉSUMÉ

On explique comment on a préparé des dérivés amide de l'aniline et de 16 chloroanilines par réaction avec les anhydrides trifluoacétique, pentafluoropropionique, heptafluorobutyrique chloracétique et dichloracétique. La séparation sur colonne capillaire a été étudiée; on présente un sommaire des données obtenues pour 85 dérivés par spectroscopie de masse - détecteur de masse sélectif. On a aussi déterminé les facteurs de réponse des amides au détecteur à capture d'électrons. L'étude comparative des cinq réactions de préparation a montré que les dérivés heptafluorobutyryl sont les plus appropriés au dosage de ce groupe d'anilines.

INTRODUCTION

Aniline is an industrial chemical of many applications. It is used to produce numerous azo dyes or dye intermediates and aniline-based pharmaceuticals. Aniline and its chlorinated analogs are also used in the manufacture of many carbamate and urea pesticides. The production of aniline in the United States totalled 823 million lbs in 1986 [1]. Since the toxicity of aniline and other aromatic amines to mammals and fish is well established [2,3], there is a need to develop analytical procedures for the determination of such compounds in toxic wastes or as contaminants in the environment.

Although the analyses of underivatized aniline and halogenated anilines have been performed by some workers using high-performance liquid-chromatography (HPLC) [4,5] with suitable detectors, others preferred to analyze aniline derivatives by gas chromatography using electron-capture and other detectors [6,7] to enhance sensitivity and/or selectivity. Among the derivatization procedures, acylation of the amino group in aromatic amines by carboxylic acid anhydrides is one of the most popular reactions, although other acylation reactions with benzyl halide reagents and alkylation reactions with substituted phenyl and benzyl halides have also been performed [6,8].

Recently, the analysis of aniline and a few other halogenated anilines using several acylation and alkylation procedures was reported by Bradway and Shafik [8]. The determination of aniline and aminophenols in aqueous solutions by a combined aceytlation and trifluoroacetylation procedure has also been demonstrated by Coutts et al. [9]. Other acylation methods for the analysis of aromatic amines using electron-capture [10] and nitrogen-selective [11] detectors were also reported. In this work, we shall describe the preparation of amide derivatives resulting from the reactions of three perfluoro anhydrides: trifluoroacetic anhydride (TFAA), pentafluoropropionic anhydride (PFPA), and heptaflurobutyric anhydride (HFBA) and two chloroacetic anhydrides: monochloroacetic anhydride (CAA) and dichloroacetic anhydride (DCAA) with aniline and 16 chloroanilines. The chloroanilines studied in this work included three monochloro-, six dichloro-, four trichloro-, and two tetrachloro- anilines as well as pentachloroaniline. See Table 1 for the complete list. A comparison of the above five types of amide derivatives in terms of their ease of formation, completeness of reaction, and interference by reaction side-products will be presented. Their mass spectral data and chromatographic properties will also be discussed.

EXPERIMENTAL

Apparatus

For GC-MS work, a Hewlett-Packard Model 5880A GC equipped with a Level 2 terminal, split/splitless injection port, a Model 5970B mass selective detector and data system was used. For GC-ECD work, a Hewlett-Packard Model 5880A GC equipped with a Level 4 terminal, split/splitless injection port and an electron-capture detector was used.

Chromatographic Conditions

MSD Analysis:

A 30 m x 0.25 mm i.d. SPB-5 (Supelco) fused silica capillary column was directly interfaced to the electron-impact ion source for maximum sensitivity. The operating temperatures (°C) were: injection port 250°, interface 280°, column initial temperature 70° (held for 0.5 min), programming rates 30°/min (from 70° to 90°) and 5°/min (from 90° to 240°). Carrier gas was helium and column head pressure was 4 psi. Septum purge flow was 1.5 mL/min. Splitless valve was on for 0.5 min after a 1 μL sample was injected in the splitless mode using the hot needle technique [12].

ECD Analysis:

A 30 m x 0.25 mm i.d. DB-5 (J and W. Scientific Co.) fused silica capillary column was used. The operating temperature (°C) were: injection port 250°, detector 300°, column initial temperature 70° (held for 0.5 min), programming rates 30°/min (from 70° to 140°), 1°/min (from 140° to 160°) and 10°/min (from 160° to 240°). Carrier gas was helium with a column head pressure of 10 psi and linear velocity of 27 cm/sec at 240°C. Makeup gas for ECD was argon/methane (95 + 5) with a flow rate of 25 mL/min. Septum purge flow was 1.5 mL/min. Splitless time was 0.5 min and 2μL injections were made manually as per MSD analysis.

Mass Spectral Data Acquisiton

Full scan EI-GC-MS data were obtained by scanning the MSD from m/z 50 to 500 at a rate of 0.95 scans per second and a scan threshold of 1000. The electron energy and electron multiplier voltage were 70 eV and 2000 V, respectively.

Materials

Chloroanilines:

Aniline and all chloroanilines except pentachloroaniline were obtained from Aldrich (Milwaukee, Wisconsin, USA). Pentachloroaniline was obtained from Riedel-de Haen through Caledon (Georgetown, Ontario, Canada). Stock solutions of individual chloroaniline at 1000 μg/mL were prepared in methanol. A mixture of all 17 anilines each at 20 μg/mL was also prepared in methanol and used for the synthesis of amide derivatives.

Anydrides:

TFAA, PFPA, and HFBA were purchased from Pierce (Rockford, Illinois, USA). CAA and DCAA were obtained fom Aldrich.

Solvents:

All solvents were distilled-in-glass grade available from Burdick and Jackson.

Phosphate buffer:

A 0.05 M solution was prepared by dissolving potassium dihydrogen phosphate (0.025 mole) and sodium dihydrogen phosphate (0.025 mole) in 1 L of organics-free water.

Derivatization of Anilines

A 0.5 mL aliquot of the 17-aniline mixture was transferred to a 15 mL centrifuge tube. After the solvent (methanol) was evaporated and replaced by 100 µL of benzene, 100 µL of the anhydride (except CAA) was added. For the CAA reactions, 500 µL of a saturated solution of chloroacetic anhydride in benzene was used. The contents were mixed well by a vortex mixer and were allowed to stand at 22°C (room temperature) or 60°C. The optimal reaction conditions were: (a) 15 min at 22°C for TFAA, (b) 2 hr at 22°C for PFPA, (c) 30 min at 60°C for HFBA, (d) 60 min at 60°C for CAA, and (e) 16 hr at 22°C for DCAA. In all cases, the reaction mixture was sealed with a tightly-capped ground glass stopper to prevent losses. After the reaction time had elapsed, 4 mL of the above phosphate buffer was added to the reaction mixture. Since TFAA reacts violently with water, addition of the aqueous buffer must be very slow. The amide derivatives of chloroanilines were isolated by extracting the mixture twice with 4 mL of benzene. The combined organic extract was passed through a 5 cm anhydrous sodium sulfate column prepared in a Pasteur pipette. After water removal, the solvent was evaporated and replaced by 1 mL of iso-octane using a gentle stream of nitrogen and a water bath of 60°C. This solution was ready for MSD anlaysis or for further column cleanup, if required (see later discussion). For ECD analysis, a 1:100 dilution of the above solution with iso-octane was made before injection into the GC.

Column Cleanup

Cleanup of amide derivatives of chloroanilines was achieved with a 1 g 5% deactivated silica gel column prepared in a disposable Pasteur pipette. After the column was washed with 5 mL of hexane, a 500 µL aliquot of the concentrated sample in iso-octane was applied to the column. After a pre-elution of the column with 5 mL of hexane, quantitative recovery of the amides was obtained by eluting with 10 mL of benzene.

RESULTS AND DISCUSSION

Derivatization of Anilines

Although the derivatization of anilines requires extra manipulation in the analytical procedure, the resulting amide derivatives have the benefits of being more stable and amenable to column cleanup than the parent compounds. The formation of derivatives with perfluoro and chloro substitution can further enhance the detection limits of the non-chlorinated as well as the mono- and di- chloroanilines when an electron-capture detector is used. In order to compare the chromatographic properties and to select the most desirable amide derivatives of the present group of anilines, their reactions with three commonly used perfluoro carboxylic acid anhydrides as well as chloro- and dichloro- acetic anhydrides were evaluated.

Among all the anhydrides tested, TFAA was the most reactive. In fact, the TFAA reaction was complete in 5 min at room temperature with all anilines except for pentachloroaniline (ca. 70% reacted) and for 2,3,5,6-tetrachloroaniline (ca. 85% reacted). Quantitative formation of the trifluoro derivatives of all anilines was achieved in 15 min. Acylation of anilines with PFPA was also fast. Maximum yields of the PFPA derivatives were obtained in 15 min for all anilines but pentachloroaniline and 2,3,5,6-tetrachloroaniline, although complete reaction for the above two anilines would require 2 hr at room temperature. Among the three perfluoro anhydrides, HFBA was the slowest to react with anilines. Nevertheless, quantitative yields of all heptafluoro derivatives was achieved in 18 hours. However, the same reaction was complete in 30 min if the reaction temperature was raised to 60°C.

Although chloroacetic anhydride reacted readily with most anilines, its reactions with 2,3,5,6-tetrachloroaniline and pentachloroaniline were far from complete even after an 18-hr reaction period at room temperature or a 60-min reaction at 60°C. The reaction of dichloroacetic anhydride with all anilines proceeded to completeness in 18 hr at room temperature.

Cleanup

The reaction products of chloroanilines and the three perfluoro anhydrides were sufficiently free of interference for subsequent analysis and, unless a determination of anilines at low levels by an ECD was performed, no further cleanup was required. However, more side-products were experienced with the CAA and especially the DCAA reactions so that the silica gel column cleanup described above was necessary to improve the quality of the chromatograms.

GC Separation of Aniline Derivatives

As shown in Figures 1 to 5, separation of the perfluoro and chloro amide derivatives of the 17 anilines on a 30 m SPB-5 column was satisfactory. For the heptafluorobutyryl (Figure 3) and the dichloroacetyl (Figure 5) derivatives, complete resolution of all aniline derivatives was achieved. However, the pentafluoropropionyl derivatives of 2,3,4- and 2,4,6- trichloroanilines (Figure 2) as well as the monochloroacetyl derivatives of 2,4- and 2,6- dichloroanilines (Figure 4) were unresolved. Similarly, two pairs of the trifluoroacetyl derivatives, namely 3-chloroaniline and 2,4-dichloroaniline together with 4-chloroaniline and 2,5-dichloroaniline, were also unresolved (Figure 1). The same order of elution and similar resolution of the amide derivatives were obtained when a 30 m DB-5 column was used. Attempts on other fused silica capillary columns such as a 25 m OV-1 and a 15 m OV-17 column were also made, however, less number of resolvable peaks was observed with these columns than the SPB-5 or DB-5 column. Thus the OV-1 and OV-17 columns were not further evaluated.

Other than a few exceptions noted below, the order of elution on the SPB-5 or DB-5 column for all amide derivatives with the same level of chlorination on the ring was very similar. For instance, the first and the last derivatives eluted were always those of aniline and pentachloroaniline, respectively. For the monochloroanilines, the order of elution was invariably in the sequence of 2-, 3-, and 4-. For the dichloroanilines, the elution order was always 2,4-, 2,5-, 2,3-, 2,6-, 3,5-, and 3,4- except that the chloroacetyl derivatives of 2,4- and 2,6- dichloroanilines coeluted. All derivatives of the trichloroanilines chromatographed in the order of 2,4,5-, 2,3,4- and 3,4,5-, although the amides of 2,4,6-trichloroaniline emerged at different places for different derivatives. The order of elution for the tetrachloroanilines was 2,3,4,5- followed by 2,3,5,6- for the three perfluoro derivatives, however, the order of elution was reversed in the cases of the monochloroacetyl and dichloroacetyl derivatives.

EI-GC-MS Data

Although diacylated derivatives have been reported for aniline and benzylamine [9], mass spectral data of all derivatives prepared in this work were consistent with a monoacylated structure. Under electron-impact (EI) conditions, perfluoro amide derivatives of the 17 anilines exhibited most or all of the following characteristic fragmentation ions: the molecular ion $(M^{+\bullet})$, $(M\text{-}C\ell)^+$, $(M\text{-}C_nF_{2n+1})^+$ and $(M\text{-}COC_nF_{2n+1})^+$ where n = 1 to 3. In addition, m/z 69 $(CF_3{}^+)$ was observed for all three perfluoro derivatives of anilines while m/z 119 $(C_2F_5{}^+)$ and m/z 169 $(C_3F_7{}^+)$ were present for all PFPA and HFBA derivatives, respectively. The observation of the above ions was consistent with the EI mass spectra reported by other workers on the amide derivatives of aromatic amines [8,9,10].

It was noted that for the perfluoro derivatives of anilines without a chlorine substitution at the ortho- positions (e.g., aniline, 3- and 4- chloroaniline, 3,4- and 3,5- dichloroaniline, 3,4,5-trichloroaniline, etc.), the M^+ is either the base peak or the second most intense peak in their mass spectra. The corresponding $(M-C_nF_{2n+1})^+$ and $(M-COC_nF_{2n+1})^+$ fragments, resulted from simple cleavages at both sides of the carbonyl group, were also intense. However, for those anilines with a 2-chloro substitution, the base peaks were always the $(M-C\ell)^+$ fragments resulted from elimination of an ortho chlorine atom from the molecular ion. Meanwhile, the intensity for M^+ was relatively weak for chloroanilines with a chlorine substitution at one of the ortho positions and very weak for those bearing chlorine atoms at both ortho positions. See Tables 1, 2, and 3 for a listing of the mass number and relative abundance of the characteristic ions for the trifluoroacetyl, pentafluoropropionyl, and heptafluorobutyrl derivatives, respectively.

While the molecular ion and the characteristic ions $(M-C\ell)^+$, $(M-COCH_2C\ell)^+$ and $(M-COCHC\ell)^+$ were observed for most chloroacetyl derivatives of anilines, the $(M-COCH_2C\ell)^+$ fragment was absent. For these derivatives, the base peak was either the $(M-C\ell)^+$ or the $(M-COCHC\ell)^+$ ion and the $M^{+\bullet}$ was either very weak or absent for those chloroanilines with chlorine with chlorine substitution at both ortho positions. Again, the intensity for the $(M-C\ell)^+$ ion was very weak for those derivatives without a chlorine substitution at the ortho positions. In addition to the $CHC\ell_2^+$ species (m/z 83 and 85), the molecular ion and characteristic ions such as $(M-C\ell)^+$, $(M-CHC\ell_2)^+$, and $(M-COCHC\ell_2)^+$ resulted from similar fragmentation pattern as the perfluoro derivatives, were observed for all dichloroacetyl derivates of anilines. With only a minor exception in 2,4-dichloroaniline, the base peak of these dichloroacetyl derivatives was either the $(M-C\ell)^+$ or the $(M-CHC\ell_2)^+$ fragment. Similar to the other derivatives, the $M^{+\cdot}$ is usually weak for those aniline derivatives with chlorine substitution at both ortho positions. The mass number and relative abundance of the characteristic ions for chloroacetyl and dichloroacetyl derivatives of anilines are listed in Table 4 and 5, respectively.

Other fragmentation masses common to all types of derivatives with the same number of ring-substituted chlorine atoms were: m/z 65 ($C_5H_5^+$) for all aniline derivatives, m/z 99 ($C_5H_4C\ell^+$) for all 2-, 3-, and 4- chloroaniline derivatives, m/z 133 ($C_5H_3C\ell_2^+$) for all dichloroaniline derivatives, m/z 167 ($C_5H_2C\ell_3^+$) for all trichloroaniline derivatives, m/z 203 ($C_5HC\ell_4^+$) for all tetrachloroaniline derivatives and m/z 237 ($C_5C\ell_5^+$) for all pentachloroaniline derivatives. It should be noted that, for the sake of simplicity, only the mass of the highest abundance in each chlorine cluster of the polychloro species was used in the discussion and tables. The fragment $C_6H_{5-n}C\ell_n^+$ (n = 0 to 5) resulting from the cleavage between the nitrogen and aromatic ring was also detected in many derivatives. In this respect, the ion $C_6H_5^+$ (m/z 77) was very prominent for all derivatives of aniline. The abundance of the ions $C_6H_4C\ell^+$ (m/z 111, monochloroanilines), $C_6H_3C\ell_2^+$ (m/z 145, dichloroanilines) and $C_6H_2C\ell_3^+$ (m/z 179, trichloroanilines) was mostly less than 20% of their corresponding base peaks. As a general rule, these ions were more prominent for those anilines without a chlorine substitution at the ortho position. The ions $C_6HC\ell_4^+$ (m/z 215, tetrachloroanilines) and $C_6C\ell_5^+$ (m/z 249, pentachloroaniline) were either very weak or absent.

ECD Response Factors of Derivatives

One of the reasons why these fluoro and chloro derivatives were prepared for the analysis of anilines was their ECD sensitivities. For a comparison of ECD response, response factors of all aniline derivatives, relative to that of 2,3,4,5-tetrachloroaniline, the most responsive member of the group, were calculated for each type of derivative and shown in Table 6. Variation in the relative response factors within the same type of derivative was less than a factor of 4 for the PFPA, HFBA, and DCAA derivatives. Formation of such derivatives thereby enhanced the detection of anilines with no or only one chlorine substitution to a sensitivity level similar to those of polychlorinated anilines. However, the same did not apply to the TFAA and CAA derivatives of aniline, as these compounds were over 100 times less sensitive to the ECD than the corresponding 2,3,4,5-tetrachloroaniline derivatives. Also included in Table 6 were the relative response factors of hexachlorobenzene so that comparison of the response factors between different types of derivatives could also be made.

Conclusions

Considering all aspects such as the ease and completeness of reaction, GC resolution, ECD sensitivity, and freedom of side-products and interference, the HFBA reaction is the derivatization technique of choice for the present group of anilines. These derivatives also produced intense molecular ions and or characteristic ions suitable for confirmation and quantitation by GC-MSD. If a column can be found to resolve the PFPA derivatives of 2,3,4- and 2,4,6- trichloroanilines or the simultaneous analysis of these two anilines is not required, the faster PFPA reaction would have been a better choice than the HFBA reaction. Although the TFAA derivatives of aniline is too insensitive for its ECD determination, this reaction may still be useful for the analysis of other chloroanilines provided that the GC resolution of the derivatives does not present a problem as mentioned before. Although they are all sensitive, the DCAA derivatives of anilines are generally less suitable for ECD analysis than the perfluoro derivatives because of the amount of interferring side-products present in the reaction mixture. Among all the anhydrides tested in this work, CAA is considered as the least satisfactory reagent for the 17 anilines since it suffers from the disadvantages such as incomplete reaction for some chloroanilines, presence of interferring side-products, and low ECD sensitivity for the derivatives of aniline and monochloroanilines.

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List of Figures

TABLE 1

Mass number (m/z) and relative abundance (%) of some characteric ions observed for the TFAA derivatives of anilines under EI conditions

Parent Aniline	$M^{+\bullet}$	$(M-C\ell)^+$	$(M-CF_3)^+$	$(M-COCF_3)^+$	Others
Aniline	189/100	-	120/85	92/58	77/64 , 65/39
2-chloro	223/37	188/100	154/13	126/42	99/25
3-chloro	223/100	-	154/77	126/64	99/24
2,4,-Dichloro	257/34	222/100	188/8	160/50	133/35
4-Chloro	223/100	-	154/35	126/74	99/26
2,5-Dichloro	257/17	222/100	188/5	160/13	133/19
2,3-Dichloro	257/33	222/100	188/11	160/29	133/24
2,6-Dichloro	256/9	222/100	188/6	160/28	133/23
3,5-Dichloro	257/94	-	188/100	160/62	133/27
2,4,5-Trichloro	293/38	256/100	222/6	196/34	167/33
2,4,6-Trichloro	291/19	256/100	222/7	196/35	169/24
2,3,4-Trichloro	291/35	256/100	222/6	196/34	167/22
3,4-Dichloro	257/100	-	188/67	160/87	133/85
2,3,4,5-Tetrachloro	327/39	292/100	258/5	230/27	203/33
2,3,5,6-Tetrachloro	327/8	292/100	258/6	230/13	203/26
3,4,5-Trichloro	293/100	-	222/61	196/88	167/22
Pentachloro	361/12	326/100	292/4	264/16	237/29

TABLE 2

Mass number (m/z) and relative abundance (%) of some characteristic ions observed for the PFPA derivatives of anilines under EI conditions

Parent Aniline	$M^{+\bullet}$	$(M-C\ell)^+$	$(M-C_2F_5)^+$	$(M-COC_2F_5)^+$	Others
Aniline	239/100	-	120/93	92/46	77/71 , 65/22
2-chloro	273/26	238/100	154/8	126/26	99/10
3-chloro	273/100	-	154/91	126/44	99/14
4-chloro	273/100	-	154/52	126/84	99/18
2,4-Dichloro	307/27	272/100	188/8	160/34	133/15
2,5-Dichloro	307/15	272/100	188/6	160/12	133/12
2,3-Dichloro	307/17	272/100	188/7	160/15	133/10
2,6-Dichloro	307/5	272/100	188/5	160/13	133/10
3,5-Dichloro	307/100	272/1	188/95	160/42	133/17
2,4,5-Trichloro	341/16	306/100	222/7	194/18	169/14
3,4-Dichloro	307/100	272/1	188/59	160/67	133/17
2,3,4-Trichloro	341/17	306/100	222/8	196/22	169/13
2,4,6-Trichloro	341/9	306/100	222/6	194/19	169/13
2,3,4,5-Tetrachloro	375/13	340/100	256/6	230/18	203/15
3,4,5-Trichloro	341/100	306/1	222/58	196/62	169/14
2,3,5,6-Tetrachloro	375/3	340/100	256/4	230/8	203/10
Pentachloro	411/6	376/100	292/5	264/13	237/17

TABLE 3

Mass number (m/z) and relative abundance (%) of some characteric ions observed for the HFBA derivatives of anilines under EI conditions

Parent Aniline	$M^{+\cdot}$	$(M-Cl)^+$	$(M-C_3F_7)^+$	$(M-COC_3F_7)^+$	Others
Aniline	289/100	-	120/88	92/53	77/69, 65/27
2-chloro	323/16	288/100	154/12	126/31	99/16
3-chloro	323/77	288/1	154/100	126/66	99/27
4-Chloro	323/91	288/1	154/59	126/100	99/33
2,4-Dichloro	357/23	322/100	188/10	160/42	133/23
2,5-Dichloro	357/14	322/100	188/7	160/22	132/18
2,3-Dichloro	357/16	322/100	188/9	160/28	133/14
2,6-Dichloro	357/3	322/100	188/5	160/25	133/13
3,5-Dichloro	357/76	322/2	188/100	160/73	133/22
2,4,5-Trichloro	391/22	356/100	222/8	196/40	169/29
3,4-Dichloro	357/90	322/2	188/85	160/100	133/33
2,3,4-Trichloro	391/21	356/100	222/9	196/42	169/22
2,4,6-Trichloro	391/10	356/100	222/4	196/31	169/19
2,3,4,5-Tetrachloro	427/19	392/100	258/8	230/33	203/23
3,4,5-Trichloro	391/87	356/2	222/94	196/100	169/43
2,3,5,6-Tetrachloro	427/2	392/100	258/6	230/20	203/26
Pentachloro	461/6	426/100	292/5	264/26	237/28

TABLE 4

Mass number (m/z) and relative abundance (%) of some characteric ions observed for the CAA derivatives of anilines under EI conditions

Parent Aniline	$M^{+\cdot}$	$(M-C\ell)^+$	$(M-CH_2C\ell)^+$	$(M-COCHC\ell)^+$	Others
Aniline	169/71	134/3	120/55	93/100	77/43,65/35
2-chloro	203/21	168/100	154/9	127/99	99/24
3-chloro	203/43	168/2	154/28	127/100	99/13
4-Chloro	203/37	168/1	154/15	127/100	99/17
2,6-Dichloro	237/2	202/100	188/5	161/92	133/20
2,4-Dichloro	237/20	202/62	188/4	161/100	133/27
2,5-Dichloro	237/15	202/100	188/6	161/88	133/32
2,3-Dichloro	237/22	202/100	188/8	161/93	133/32
3,5-Dichloro	237/37	202/3	188/25	161/100	133/18
2,4,6-Trichloro	273/6	236/72	224/2	195/100	169/23
3,4-Dichloro	237/27	202/1	188/11	161/100	133/13
2,4,5-Trichloro	273/29	236/90	224/4	195/100	169/30
2,3,4-Trichloro	273/32	236/81	224/5	197/100	167/25
2,3,5,6-Tetrachloro	-	272/100	258/2	231/68	203/21
3,4,5-Trichloro	273/36	236/2	224/9	197/100	167/12
2,3,4,5-Tetrachloro	307/27	272/100	258/4	231/80	203/27
Pentachloro	-	306/100	-	265/88	237/21

TABLE 5

Mass number (m/z) and relative abundance (%) of some characteric ions observed for the DCAA derivatives of anilines under EI conditions

Parent Aniline	$M^{+\bullet}$	$(M-C\ell)^+$	$(M-CHC\ell_2)^+$	$(M-COCHC\ell_2)^+$	Others
Aniline	203/31	168/1	120/100	92/36	77/41,65/27
2-chloro	237/23	202/79	154/100	126/82	99/44
3-chloro	237/27	202/1	154/100	126/40	99/17
4-Chloro	237/33	202/2	154/100	126/68	99/27
2,4-Dichloro	273/38	236/76	188/97	160/100	133/58
2,5-Dichloro	273/29	236/100	188/96	160/74	133/70
2,3-Dichloro	273/33	236/78	188/100	160/78	133/51
2,6-Dichloro	273/7	236/100	188/84	160/85	133/50
3,5-Dichloro	273/28	236/1	188/100	160/39	133/19
3,4-Dichloro	273/35	236/2	188/100	160/56	133/22
2,4,6-Trichloro	307/14	272/100	222/73	194/99	167/53
2,4,5-Trichloro	307/46	272/100	222/99	194/90	167/60
2,3,4-Trichloro	307/45	272/90	222/100	194/96	167/45
3,4,5-Trichloro	307/36	272/2	222/100	194/51	167/16
2,3,5,6-Tetrachloro	341/1	306/100	258/27	230/28	203/28
2,3,4,5-Tetrachloro	341/31	306/100	258/63	230/64	203/49
Pentachloro	375/5	340/100	292/33	264/44	237/42

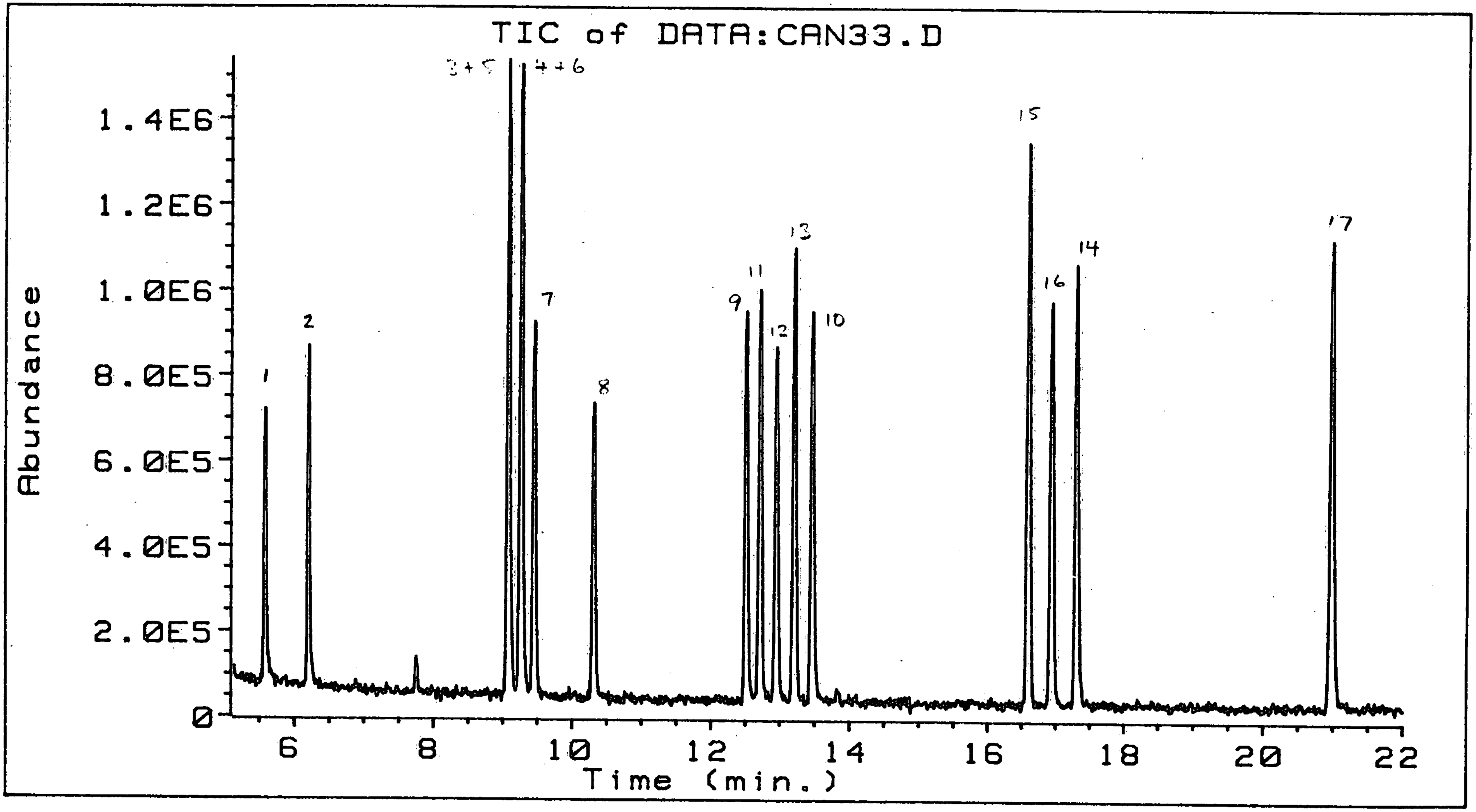
TABLE 6

Relative response factors of various amide derivatives of anilines by electron-capture detection[1]

Parent Aniline	TFAA	PFPA	HFBA	CAA	DCAA
Aniline	<0.1	3.9	3.3	<0.1	3.3
2-chloro	1.1	3.9	3.6	1.3	3.7
3-chloro	1.4	5.4	5.1	1.4	4.5
4-Chloro	1.7	6.5	6.4	1.7	5.1
2,4-Dichloro	2.3	5.3	5.5	5.6	6.1
2,5-Dichloro	1.8	6.2	6.1	4.7	5.9
2,3-Dichloro	2.1	6.1	6.6	5.2	6.2
2,6-Dichloro	1.3	2.9	3.6	2.6	4.9
3,5-Dichloro	6.2	6.0	5.9	4.4	5.4
2,4,5-Trichloro	4.0	5.4	5.5	5.5	6.1
3,4-Dichloro	6.7	7.4	7.5	3.8	5.6
2,3,4-Trichloro	4.2	7.5	9.0	6.6	8.3
2,4,6-Trichloro	4.0	6.2	5.2	5.2	6.0
2,3,4,5-Tetrachloro	10.0	10.0	10.0	10.0	10.0
3,4,5-Trichloro	7.7	8.1	8.6	7.2	6.1
2,3,5,6-Tetrachloro	7.3	7.4	7.6	-[2]	7.8
Pentachloro	9.1	8.7	8.4	-[2]	9.2
Hexachlorobenzene	10.1	9.3	10.8	7.8	9.8

[1]Response factors relative to the derivative of 2,3,4,5-tetrachloroaniline

[2]Relative response factors not calculated because of incomplete reaction


TIC of DATA:CAN33.D
Abundance
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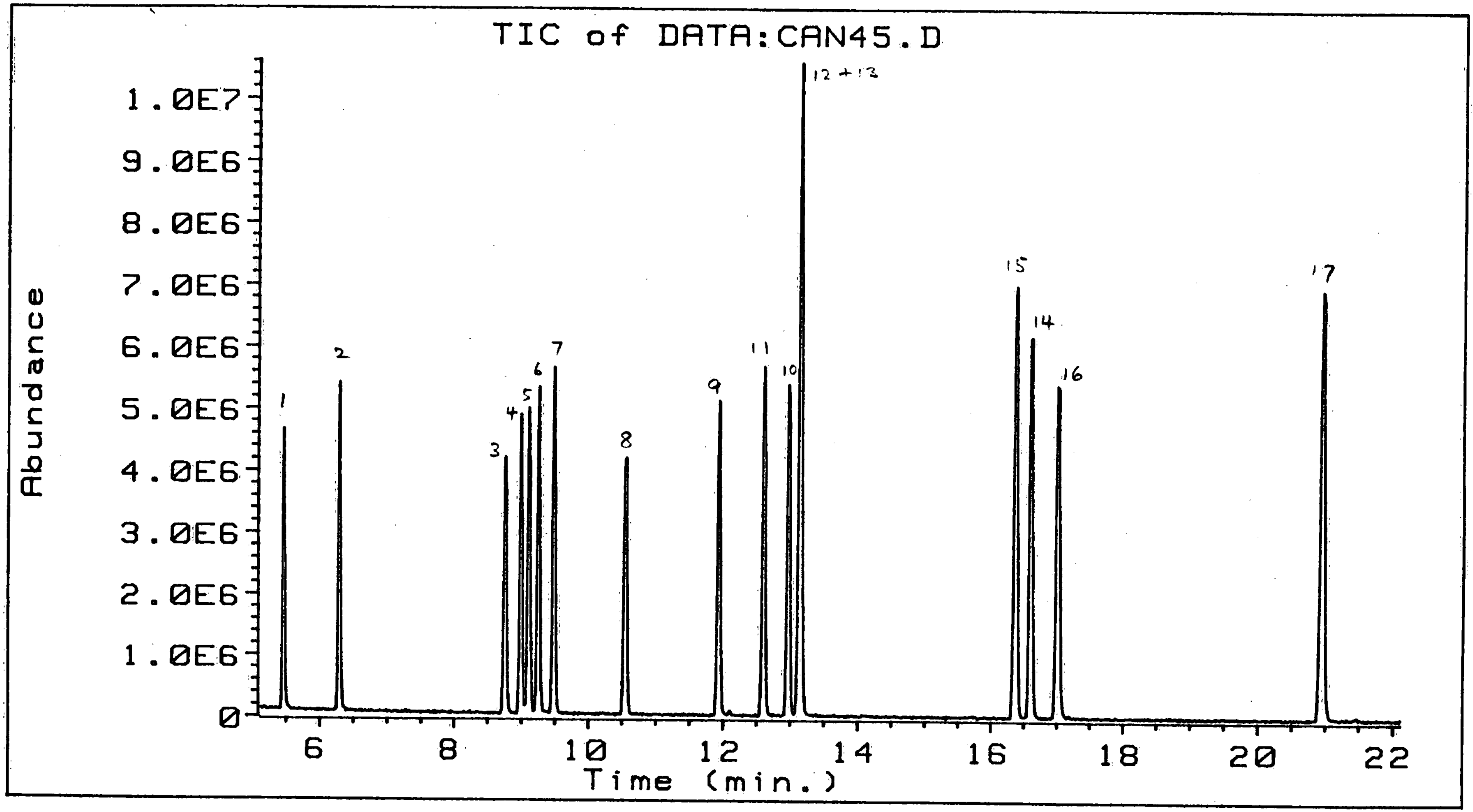
1.2E6
1.0E6
8.0E5
6.0E5
4.0E5
2.0E5
0
6
8
10
12
14
16
18
20
22
Time (min.)
1
2
3+5
4+6
7
8
9
11
12
13
10
15
16
14
17

Figure 1.



TIC of DATA:CAN45.D
Abundance
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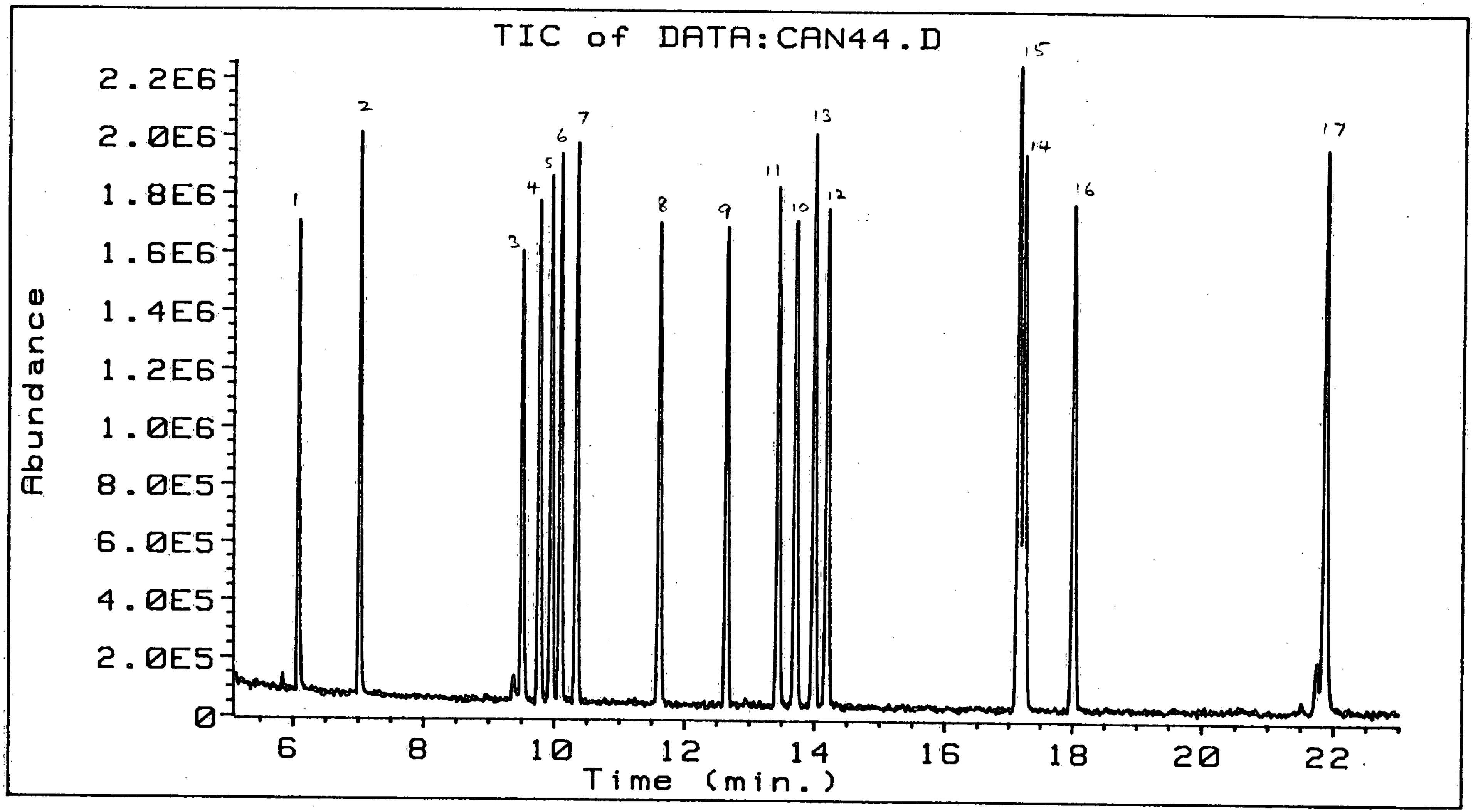
8.0E6
7.0E6
6.0E6
5.0E6
4.0E6
3.0E6
2.0E6
1.0E6
0
6
8
10
12
14
16
18
20
22
Time (min.)
1
2
3
4
5
6
7
8
9
11
10
12 + 13
15
14
16
17

Figure 2.


TIC of DATA:CAN44.D
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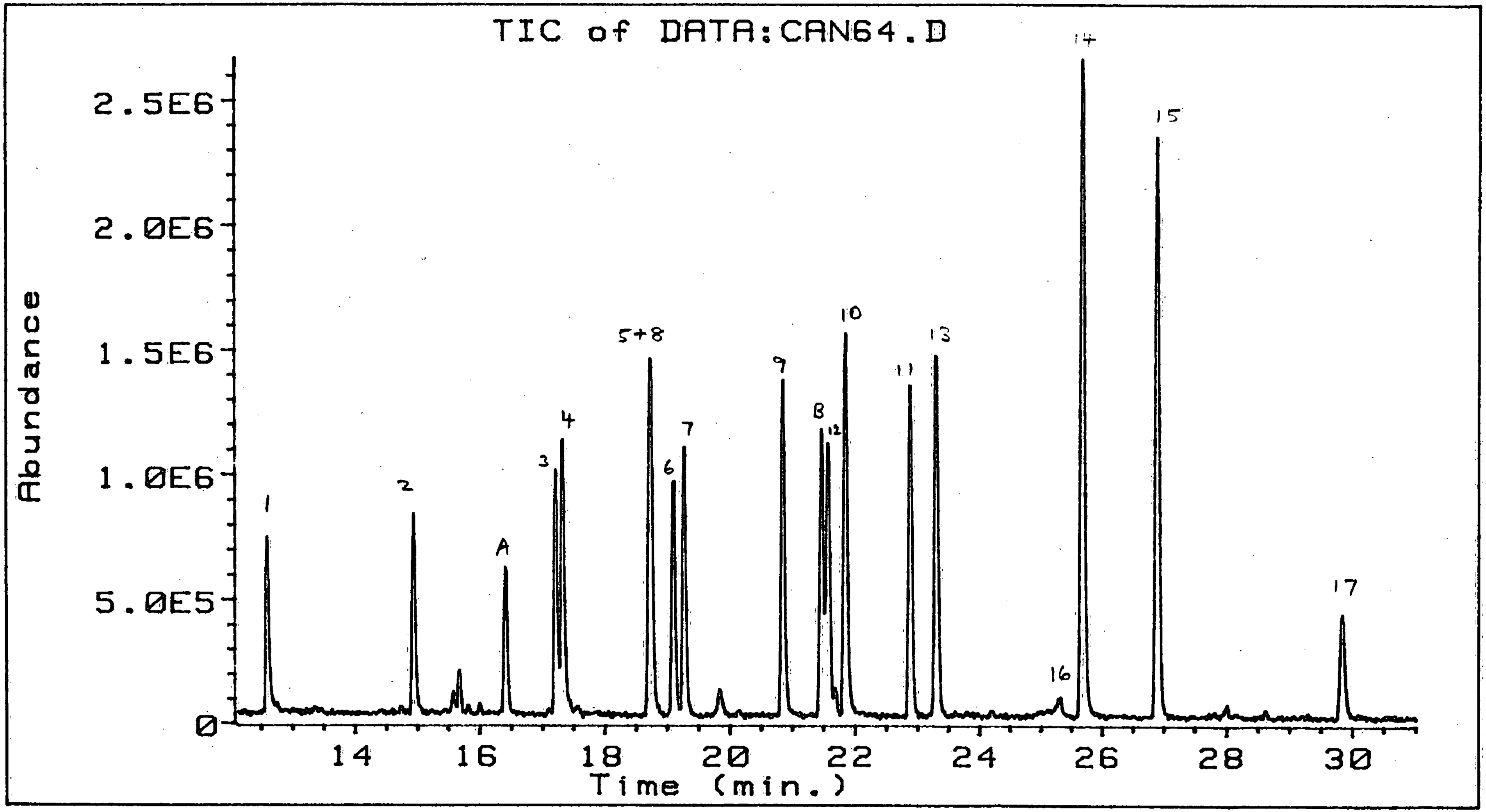
1.8E6
1.6E6
1.4E6
1.2E6
1.0E6
8.0E5
6.0E5
4.0E5
2.0E5
0
6
8
10
12
14
16
18
20
22
Time (min.)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

Figure 3.


TIC of DATA:CAN64.D
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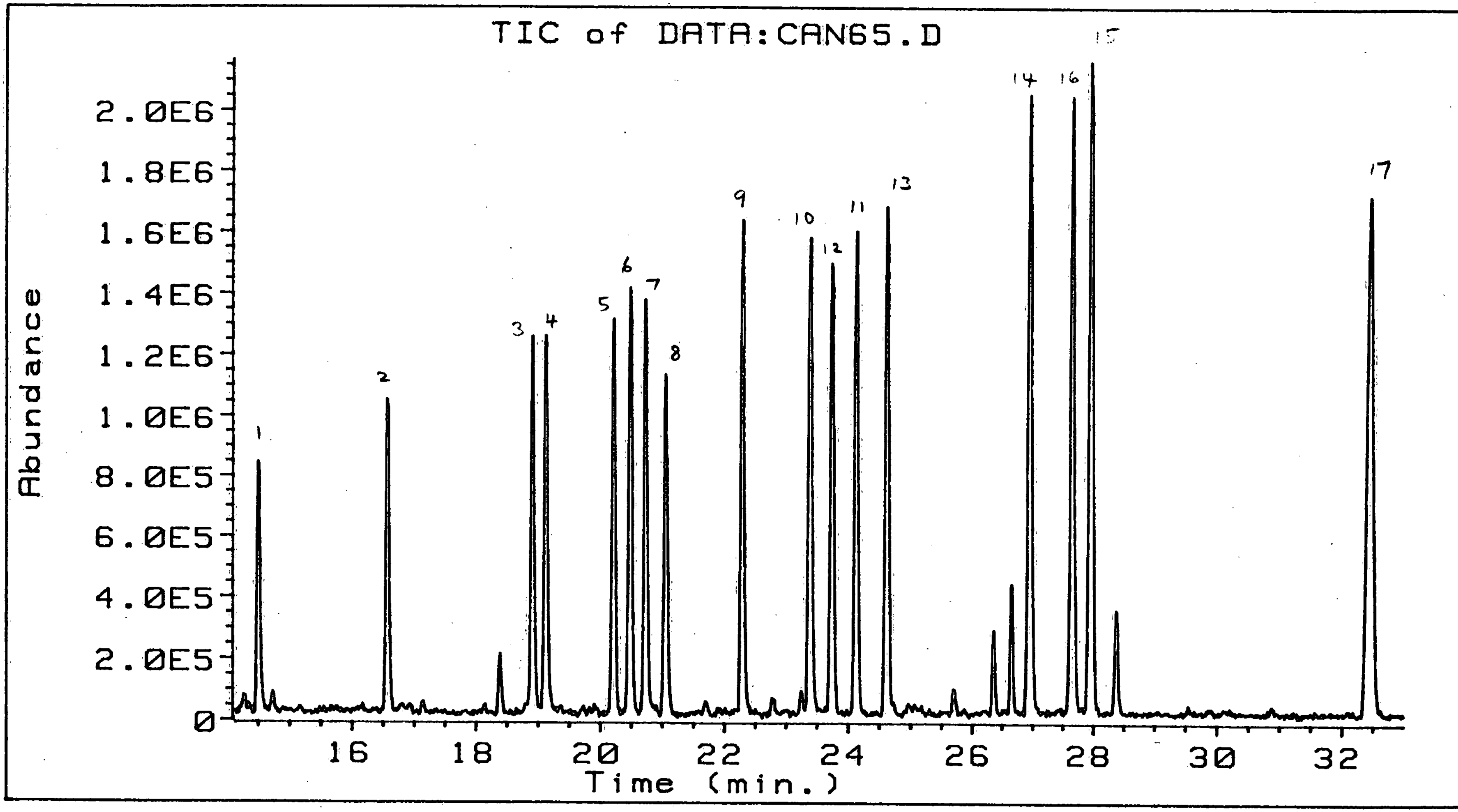
1.5E6
1.0E6
5.0E5
0
14
16
18
20
22
24
26
28
30
Time (min.)
1
2
A
3
4
5+8
6
7
9
B
12
10
11
13
16
14
15
17

Figure 4.


TIC of DATA:CAN65.D
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1.6E6
1.4E6
1.2E6
1.0E6
8.0E5
6.0E5
4.0E5
2.0E5
0
16
18
20
22
24
26
28
30
32
Time (min.)
1
2
3
4
5
6
7
8
9
10
12
11
13
14
16
15
17

Figure 5.