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# ANALYSIS OF PHENOLS BY CHEMICAL DERIVATIZATION. V. DETERMINATION OF PENTACHLOROPHENOL AND 19 CHLORINATED PHENOLS IN SEDIMENTS

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## MANAGEMENT PERSPECTIVE

In response to a request from Water Quality Branch, Atlantic Region, a method for the quantitative analysis of chlorophenols in sediments was developed. This method exceeds the requirements of the original request since it not only applies to the analysis of pentachlorophenol but also to 19 other chlorophenols. Many of these chlorophenols are toxic chemicals and are listed as US EPA priority pollutants. This multi-residue method is cost-effective since it was designed so that analysis of other classes of compounds can be included as future needs arise.

**ABSTRACT**

A method for the quantitative and isomer-specific analysis of pentachlorophenol and 19 chlorophenols in sediment was developed. After acidification to pH < 1, sediment samples were soxhlet extracted with a 59/41 (v/v) acetone/hexane mixture for 20 hr. Phenols in the organic extract were back extracted into 2% $KHCO_3$ and were then acetylated with acetic anhydride and extracted by petroleum ether. After evaporation to a small volume, the acetates were cleaned up on a 5% deactivated silica gel column. The extracts were then analyzed on a 12 m OV-1 column interfaced to an electron-capture detector and on a 30 m SPB-5 column interfaced to a mass selective detector. The procedure has been validated with sediment samples fortified at 100, 10 and 1 ng/g levels of chlorophenols. Recoveries of dichloro- and the higher chlorophenols were generally between 80 and 95% at all three levels of fortification while recoveries of monochlorophenols were between 65 and 85%. The two chloromethylphenols were less than 50% recovered. Using a 50 g sample size, the estimated method detection limit was ca. 0.2 ng/g.

**SOMMAIRE**

On a mis au point une méthode permettant d'effectuer l'analyse quantitative et isomérique du pentachlorophénol et de 19 chlorophénols contenus dans les sédiments. Après avoir acidifié le pH des échantillons de sédiments à moins de 1, on procède à une extraction au soxhlet d'une durée de vingt heures au moyen d'un mélange d'acétone et d'hexane ayant un rapport volumique de 59/41. Les phénols renfermés dans l'extrait organique sont soumis à une seconde extraction dans une solution de $KHCO_3$ de 2 p. 100 et ensuite acétylés à l'anhydride acétique et extraits à la benzoline. Après réduction du volume par évaporation, les acétates sot purifiés à l'aide d'une colonne de gel de silice désactivé à 5 p. 100. L'analyse des extraits se fait au moyen d'une colonne OV-1 de 12 m reliée à un détecteur à capture d'électrons et également d'une colonne SPB-5 de 30 m reliée à un détecteur de masse sélectif. Cette méthode a été validée pour des échantillons de sédiments dont on a rehaussé la teneur en chlorophénols de 100, 10 et 1 ng/g. Pour les trois concentrations précitées, le taux de récupération des chlorophénols comprenant deux atomes de chlore ou plus varient entre 80 et 95 p. 100 tandis qu'il oscille entre 65 et 85 p. 100 pour les chlorophénols simples. Moins de la moitié des chlorométhylphénols ont été récupérés. Pour un échantillon de 50g, on estime que le seuil de détection de la méthode est d'environ 0,2 ng/g.

## PERSPECTIVE GESTION

Pour faire suite à la demande de la Direction de la qualité des eaux, Région de l'Atlantique, l'INRE a élaboré une méthode d'analyse quantitative des chlorophénols qui se trouvent dans les sédiments. La méthode qui est présentée dépasse de loin les exigences de la demande initiale puisqu'elle permet non seulement d'analyser les pentachlorophénols mais aussi 19 autres chlorophénols. Plusieurs d'entre eux sont toxiques et figurent parmi les polluants jugés prioritaires par l'EPA aux États-Unis. De plus, cette méthode dite à résidus multiples est économique puisqu'on pourra l'adapter à l'analyse d'autres types de composés chimiques au fur et à mesure que le besoin s'en fera sentir.

## INTRODUCTION

Pentachlorophenol (PCP) has long been used as a wood preservative and other chlorophenols are often used as precursors in the production of many phenoxyalkanoic herbicides and biocides. According to one report, over 60% of the 3200 tonnes of chlorophenols used annually in Canada is PCP (1). Residues of these phenols are reported in the environment and especially in industrial wastewaters and sludges. Because of the acute toxicity of PCP and other chlorophenols, routine methods for the monitoring of these chemicals in water and sediments are required. Analysis of chlorophenols in sediment samples are particularly important since phenols are retained in large quantities by municipal solid wastes, landfill leachates and sediments (2-4). Several papers have been published on the extraction and analysis of PCP and a few other phenols in sediments (5-9). In previous publications, we have reported methods for the isomer-specific analysis of chlorophenols in water by the formation of acetate (10), chloroacetate (11), and pentafluorobenzyl (PFB) ether (12) derivatives. Presumably because of its simplicity and ruggedness, the acetate procedure is a popular approach since it has also been used by many other workers (13-17). However, application of the acetate procedure to environmental samples is limited to phenols with two or more chlorine atoms if an electron-capture detector (ECD) is used for analysis since the ECD sensitivity for monochloro- and non-chlorinated phenol acetates is poor. Recently, analysis of chlorophenol acetates

by GC-MS has been reported (17-20). Since strong characteristic ions were observed for these acetates under electron impact (EI) conditions, GC-MS, operating in selected ion monitoring (SIM) mode is potentially a highly specific and sensitive technique for phenol analysis. The recent advent of Mass Selective Detector (MSD) and data system provided fully automated acquisition of GC-MS data at lower cost. In this paper, we shall describe a method for the routine analysis of PCP and 19 chlorophenols in sediment samples by formation of acetate derivatives followed by quantitation with GC-ECD and GC-MSD.

## EXPERIMENTAL

### Apparatus and Reagents

(a) Gas chromatograph. - Hewlett-Packard 5880A equipped with $Ni^{63}$ electron-capture detector, 7671A Autosampler, Level 4 terminal, and split-splitless capillary column injection port, GC column, 12 m x 0.2 mm i.d. fused silica capillary column coated with cross-linked dimethyl silicone gum and surface deactivated by siloxane (Hewlett-Packard part no. 19091-60312). Operating temperatures (°C): injection port 200°, detector 300°, column initial 70°, hold 0.5 min, programming rate 1, 10°/min (70° to 120°), hold 5 min at 120°, programming rate 2, 2°/min (120° to 160°). Splitless valve on for 0.5 min. Carrier gas, helium at 10 psi. Detector make-up gas, argon/methane 95+5 at 25 mL/min.

(b) Gas Chromatograph. - Hewlett-Packard 5880A equipped with 5970B mass selective detector, series 200 computer, 9133XV disc drive, a split/splitless injection port, Level 2 terminal, and 7671A Autosampler. A 30 m x 0.25 mm i.d. SPB-5 fused silica capillary column (Supelco Ltd.) was directly interfaced to the electron-impact ion source for maximum sensitivity. Electron energy 70 eV. Operating temperatures (°C): injection port 250°, interface temperature 280°, column initial 70°, hold 0.5 min, programming rate 1, 30°/min (70° to 120°), programming rate 2, 2.5°/min (120° to 180°), hold 10 min at 180°. Splitless valve on for 0.5 min. Carrier gas, helium at 4 psi. Split vent flow, 50 mL/min.

(c) Chlorophenol Standards. - Available from Aldrich Chemical Co. or Supelco, Inc. (Phenol Kit 27). 2,3,4,6-Tetrachlorophenol obtained from Eastman Organic Chemicals. Prepare all stock solutions in toluene at 5 mg/mL. Prepare mixture of phenols in acetone at 50 µg/mL for spiking purposes. Keep all solutions in the dark at 4°C.

(d) Acetic anhydride. - Distill AnalaR grade (BDH Chemicals) reagent three times and collect 138-140°C fraction for acetylation reactions.

**Fortification of Sediment Samples**

Spike 100 µL phenol mixture in acetone at appropriate concentrations to 50 g sediment. Mix well with spatula and equilibrate 30 min before extraction.

**Extraction**

Place sediment sample on top of 5 cm Celite 545 in a 45 mm i.d. glass thimble with coarse frit. Acidify samples to pH < 1 with 1+1 (v/v) $H_2SO_4$. Put thimble in a Soxhlet extractor and extract with 350 mL 59+41 (v/v) acetone/hexane for 20 hr at a rate of 6 to 8 cycles per hour. After extraction, add 50 mL 2% $KHCO_3$ (aqueous) to organic extract and evaporate solvent down to ca. 100 mL. Add 50 mL hexane to mixture to facilitate phase separation and drain aqueous layer to a 250 mL volumetric flask. Extract the organic layer with 40 mL 2% $KHCO_3$ for 2 min and drain the aqueous fraction to the above 250 mL volumetric flask. Repeat extraction twice with 30 mL base each time. After last extraction, discard organic layer. To prepare a calibration standard, spike known amounts of phenols directly to 150 mL 2% $KHCO_3$ and proceed to derivatization and cleanup procedure described below.

**Derivatization and Cleanup**

To the 150 mL 2% $KHCO_3$ solution containing phenols, add 3 mL acetic anhydride and 25 mL petroleum ether (30-60°C). Stir sample slowly until evolution of $CO_2$ subsides and then stir vigorously for 30 min. Separate layers in separatory funnel and drain water sample back into original container. Collect organic layer in 250 mL round-bottom flask. Repeat extractive acetylation twice with 3 mL acetic anhydride and 25 mL petroleum ether. Dry organic extract with anhydrous sodium sulfate. Add 2 mL isooctane and evaporate solvent down to ca. 3 mL using a three-stage Snyder column.

Prepare a mini cleanup column by plugging a long Pasteur pipet (23 x 0.5 cm i.d.) with a piece of silanized glasswool. Fill column with 5 cm 5% deactivated silica gel. Tap column gently and add 5 mm anhydrous $Na_2SO_4$ at top. Rinse column with 5 mL hexane and discard washings. With a Pasteur pipet, quantitatively transfer acetylated products to silica gel column. Elute column with 5 mL hexane and discard. Continue elution with 10 mL toluene. Collect this fraction and make up to volume. Inject 2 µL extract, in splitless mode, and analyze by GC-ECD and by GC-MSD.

**GC-MSD Analysis of Phenol Acetates**

(a) Total ion scanning. - Obtain abundance data of the major fragments for chlorophenol acetates by scanning from m/z 40 to 320 at a rate of 1.5 scans per second and a scan threshold of 10.

(b) Selected ion monitoring. - For quantitative purposes, monitor three characteristic ions for each group of phenols as shown in Table 1 and set dwell time to 100 ms for each ion. To maximize sensitivity, divide the ions into six groups or retention time windows and integrate the most abundant ion.

**RESULTS AND DISCUSSION**

In a previous paper, we have successfully demonstrated that 15 di-, tri-, tetra- and penta- chlorophenols in water samples can be conveniently analyzed in their acetate forms after an in-situ acetylation reaction (10). With a combination of a high resolution capillary column and an electron-capture detector, isomer-specific analysis of the above 15 chlorophenols was feasible and quantitative recoveries were obtained from surface water containing as low as 0.01 µg/L of the phenols. Phenol, monochlorophenols, and chloromethyl-phenols are also acetylated by the same or similar procedures. However, because the electron-capture sensitivities of these acetates are a few hundred to over 1000 times lower than that of PCP acetate (Table 2), these derivatives are normally undetected by an electron-capture detector at levels commonly found in environmental samples. A Mass Selective Detector (MSD) or other mass spectrometric detectors do not have a discriminating sensitivity effect against the non-chlorinated and monochlorinated phenols. For example, the relative

response factors of the 21 phenols determined by the MSD on the $CH_3CO^+$ ion (m/z=43) are all within a factor of 5 and within a factor of 2 with the exception of 3 phenols (Table 2). Therefore, use of a MSD will allow the analysis of non-chlorinated and monochlorinated phenols at levels similar to phenols of higher chlorination. A reconstructed total ion current chromatogram of the 21 phenol acetates is shown in Figure 1.

The mass spectrum of each chlorophenol acetate obtained under EI conditions included the following three characteristic masses: (1) the molecular ion ($M^+$), (2) the parent phenol moeity (M-42), and (3) the $CH_3CO^+$ fragment. The m/z values of characteristic masses for the 21 phenol acetate derivatives and their relative abundances are listed in Table 2. For acetates of chlorophenols, the molecular ions were low in abundance, and in all cases, they were less than 20% of their respective base peaks. In cases of phenol, the three monochlorophenols and two chloromethylphenols, the M-42 ions were the most abundant ions. For other phenols of higher chlorination, the most abundant ion was the $CH_3CO^+$ fragment.

For quantitative GC-MSD analysis of these acetate derivatives, selected ion monitoring (SIM) of the above-mentioned characteristic ions was used. Representative single ion chromatograms of phenol acetates at each level of chlorination are depicted in Figures 2A and 2B. The presence of a phenol in question was confirmed if all three characteristic ions were present at the expected retention time and at

a ratio of not more than ±20% deviation from the expected relative abundance. Once the presence of a phenol had been confirmed, the most abundant characteristic ion was used for quantitation in order to optimize sensitivity. Since chlorophenol acetates have non-overlapping retention time windows, the entire chromatogram can be subdivided into six ion groups, one for each level of chlorination corresponding to phenol through to PCP. In this case, further enhancement in sensitivity can be achieved by monitoring only three ions for those phenols expected in this window. Retention times for the acetates of the two chloromethylphenols fell into the retention time window of dichlorophenol acetates. Therefore, characteristic masses of these two groups of phenols were both monitored within this window.

Chlorophenols in sediments are generally extracted by the following three approaches: (1) extraction with an aqueous buffer solution or a base at high pH (5, 21); (2) solvent extraction after the sediment is acidified to a low pH (6-9); or (3) steam distillation of sediments acidified to pH < 1 (22, 23). All approaches provide satisfactory recoveries of PCP and/or a few other chlorophenols. In this work, sediment samples were acidified to pH $\leq$ 2 with 1+1 $H_2SO_4$ and were then soxhlet extracted with a 59+41 mixture of acetone and hexane. This technique was used because the same method produced quantitative recoveries of various classes of compounds, such as PCBs (24), chlorobenzenes (25), chlorinated insecticides (26), herbicides

(26), and PAHs (26). By using the same extraction technique, a multi-class, multi-residue method can be developed in the future.

Back extraction of chlorophenols into a base was a critical step in this method. Preliminary experiments indicated that over 90% recovery of all chlorophenols in a hexane solution could be achieved by three successive back extractions with 40+30+30 mL of 2% $KHCO_3$. Before an efficient back extraction of phenols could be performed on sediment extracts, the acetone and acids in the organic layer had to be removed. Acetone was evaporated in the presence of 50 mL 2% $KHCO_3$ using a three-stage Snyder column with a heating mantle. The base was added as a keeper for the phenols during solvent evaporation and was also used to neutralize the free acids present in the sample extract.

To enhance phase separation during back extraction, the organic extract was evaporated down to ca. 100 mL, then 50 mL of hexane was added to the concentrated extract.

Column cleanup was performed with a 5% deactivated silica gel column. Polar sediment coextractives that were not removed in the $KHCO_3$ partitioning step were removed by silica gel since they tended to stay on the column. Acetates of all chlorophenols were eluted in one fraction by 10 mL of toluene. If the analyses of monochlorophenols are not required, a less polar 1+1 toluene/hexane eluant can be used (10). If further evaporation of solvent is required, the toluene should be replaced by 5+95 acetone/hexane in the column cleanup step.

In the present work, recovery data for chlorophenols were obtained at 100, 10 and 1 ng/g levels. Sediment samples used in the

fortification experiments were prepared from a bulk, composite sediment sample by mixing, sandy, loamy and clay-based sediments in a 2:1:2 ratio. After fortification, the sediment samples were equilibrated for 30 min before acidification and soxhlet extraction. Sediment extracts were then acetylated, cleaned up and analyzed by GC-ECD and GC-MSD. At 100 and 10 ng/g levels, the extracts were sufficiently clean for reliable GC-ECD analysis of the di-, tri-, tetra-, and penta- chlorophenols. At the 1 ng/g fortification level, this cleanup procedure did not produce extracts clean enough for ECD quantitation of the dichlorophenol derivatives, although useful results could still be obtained for the higher chlorophenols. In such cases, as well as for the analysis of monochlorophenols, a Mass Selective Detector operating in the SIM mode was used to provide quantitative results.

As shown in Table 2, recoveries of tri-, tetra-, and penta-chlorophenols at all levels of validation were between 85 and 95%, whereas the dichlorophenols were between 75 and 90% recovered. Recoveries of monochlorophenols were slightly lower at 65 to 85%. On the other hand, the two chloromethylphenols were only 40 to 50% recovered and the recovery of phenol itself was erratic by this procedure. The method detection limit (27) for the 20 chlorophenols by mass selective detection in this study was estimated as 0.2 ng/g based on a 50 g sample and a final volume of 1 mL. Acetylated extracts from sediment samples fortified to 10 ng/g for each phenol as analyzed by ECD and MSD are shown in Figures 3 and 4, respectively.

The effect of storage time on the recovery of chlorophenols was briefly studied. A set of sediment samples was fortified to 10 ng/g per phenol and stored at 4°C in the dark for 4 and 8 days before extraction and analysis. No significant change was observed in the recoveries of any of the chlorophenols after 4 or 8 days of cold storage as compared to the control samples which were spiked and extracted immediately.

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**TABLE 1** **Retention time windows and characteristic ions used for selected ion monitoring of chlorophenol acetates by GC-MSD.**

| Ion Group | Corresponding Phenols | Retention Time Window, min | Characteristic Ions m/z |
|---|---|---|---|
| 1 | Phenol | 4.20 - 6.00 | 43, 94, 136 |
| 2 | Chloro- | 6.00 - 8.00 | 43, 128, 170 |
| 3 | Dichloro- and Chloromethyl- | 8.00 - 12.00 | 43, 142, 162, 184, 204 |
| 4 | Trichloro- | 12.00 - 18.00 | 43, 198, 240 |
| 5 | Tetrachloro- | 18.00 - 23.00 | 43, 232, 274 |
| 6 | PCP | 23.00 - 27.00 | 43, 266, 308 |

**TABLE 2. Characteristic ions, relative abundances and relative response factors (PCP acetate=10.0) of 21 chlorophenol acetates.**

| No. | Parent Phenol | Characteristic Ions, m/z (rel. abundance) | Rel. Response Factors | |
|---|---|---|---|---|
| | | | MSD* | ECD |
| 1 | Phenol | 43( 28), 94(100), 136 ( 10) | 4.0 | <0.01 |
| 2 | 2-Chloro | 43( 59), 128(100), 170 ( 12) | 6.5 | 0.03 |
| 3 | 3-Chloro | 43( 80), 128(100), 170 ( 16) | 7.0 | 0.03 |
| 4 | 4-Chloro | 43( 43), 128(100), 170 ( 11) | 5.4 | 0.02 |
| 5 | 2-Chloro-5-methyl | 43( 56), 142(100), 184 ( 15) | 2.2 | 0.01 |
| 6 | 2-6-Dichloro | 43(100), 162( 66), 204 ( 14) | 8.3 | 0.74 |
| 7 | 4-Chloro-3-methyl | 43( 49), 142(100), 184 ( 13) | 3.0 | 0.03 |
| 8 | 2,4-Dichloro | 43(100), 162( 99), 204 ( 11) | 6.0 | 0.83 |
| 9 | 3,5-Dichloro | 43(100), 162( 51), 204 ( 14) | 8.2 | 0.98 |
| 10 | 2,3-Dichloro | 43(100), 162( 52), 204 ( 15) | 7.0 | 0.87 |
| 11 | 3-4-Dichloro | 43( 93), 162(100), 204 ( 14) | 6.4 | 0.76 |
| 12 | 2,4,6-Trichloro | 43(100), 198( 50), 240 ( 7) | 8.4 | 3.2 |
| 13 | 2,3,6-Trichloro | 43(100), 198( 36), 240 ( 8) | 9.9 | 3.0 |
| 14 | 2,3,5-Trichloro | 43(100), 198( 40), 240 ( 10) | 7.3 | 3.2 |
| 15 | 2,4,5-Trichloro | 43(100), 198( 59), 240 ( 7) | 5.7 | 2.7 |
| 16 | 2,3,4-Trichloro | 43(100), 198( 58), 240 ( 7) | 5.7 | 4.1 |
| 17 | 3,4,5-Trichloro | 43(100), 198( 61), 240 ( 12) | 5.0 | 3.2 |
| 18 | 2,3,5,6-Tetrachloro | 43(100), 232( 39), 274 ( 12) | 10.0 | 4.5 |
| 19 | 2,3,4,6-Tetrachloro | 43(100), 232( 54), 274 ( 8) | 7.0 | 5.0 |
| 20 | 2,3,4,5-Tetrachloro | 43(100), 232( 59), 274 ( 9) | 6.2 | 7.0 |
| 21 | PCP | 43(100), 266( 51), 308 ( 10) | 10.0 | 10.0 |

*Based on ion m/z=43.

**TABLE 3. Mean % recovery of chlorophenols and standard deviations from fortified sediment samples.**

| Fortification Level, ng/g<br>No. of Replicates | 100<br>5 | 10<br>6 | 1<br>6 |
|---|---|---|---|
| Phenol | | | |
| 2-Chloro- | 73±6 | 74±7 | 74±7 |
| 3-Chloro- | 76±4 | 79±4 | 86±3 |
| 4-Chloro- | 68±6 | 77±5 | 65±8 |
| 2-Chloro-5-methyl- | 47±3 | 41±4 | 51±6 |
| 2,6-Dichloro- | 84±5 | 92±9 | 76±10 |
| 4-Chloro-3-methyl- | 42±3 | 38±4 | 50±7 |
| 2,4-Dichloro- | 80±5 | 82±6 | 88±6 |
| 3,5-Dichloro- | 78±4 | 77±11 | 83±3 |
| 2,3-Dichloro- | 89±5 | 94±8 | 87±4 |
| 3,4-Dichloro- | 76±4 | 77±12 | 85±5 |
| 2,4,6-Trichloro- | 87±4 | 87±3 | 88±5 |
| 2,3,6-Trichloro- | 90±2 | 94±3 | 83±5 |
| 2,3,5-Trichloro- | 96±2 | 93±4 | 91±3 |
| 2,4,5-Trichloro- | 91±2 | 95±4 | 87±2 |
| 2,3,4-Trichloro- | 95±2 | 94±5 | 93±2 |
| 3,4,5-Trichloro- | 83±4 | 86±6 | 91±7 |
| 2,3,5,6-Tetrachloro- | 93±5 | 90±2 | 90±4 |
| 2,3,4,6-Tetrachloro- | 91±3 | 93±3 | 94±8 |
| 2,3,4,5-Tetrachloro- | 94±2 | 95±5 | 95±5 |
| PCP | 85±5 | 92±5 | 96±4 |

**FIGURES**

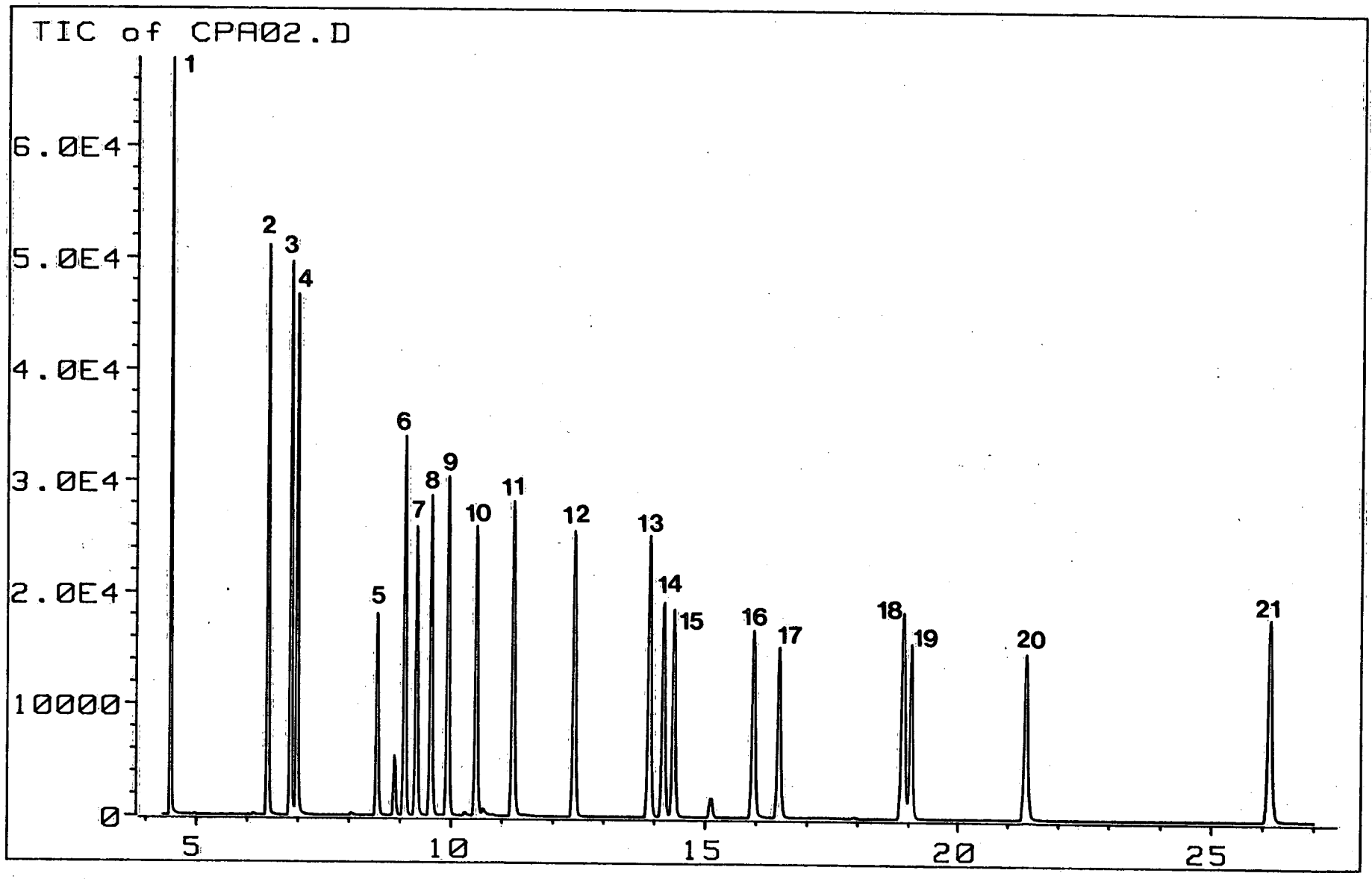
Figure 1 EI-GC-MSD total ion current trace of 21 phenol acetates as recorded on a 30 m SPB-5 column. Refer to the numbers in Table 2 for peak identification.

Figure 2A EI-GC-MSD selected ion monitoring of acetate derivatives for phenol, monochlorophenols, dichlorophenols and chloromethylphenols.

Figure 2B EI-GC-MSD selected ion monitoring of acetate derivatives for trichlorophenols, tetrachlorophenols and PCP.

Figure 3 GC-ECD chromatogram of acetylated extract from a sediment sample fortified to 10 ng/g for each phenol.

Figure 4 GC-MSD chromatogram of the same sample shown in Figure 3. Note that acetates of phenol, monochlorophenols and chloromethylphenols are easily identified by this detector.


TIC of CPA02.D
6.0E4
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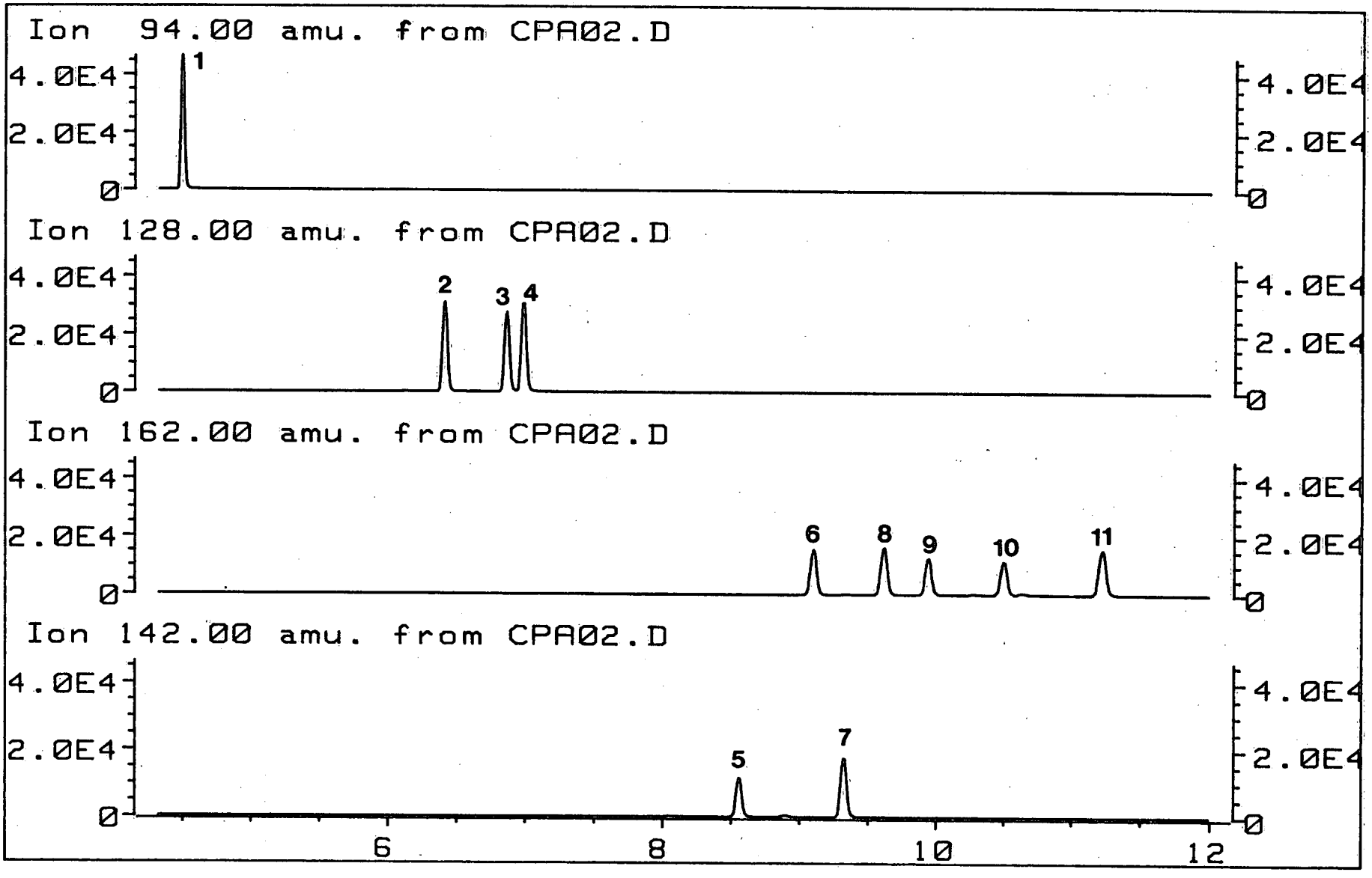
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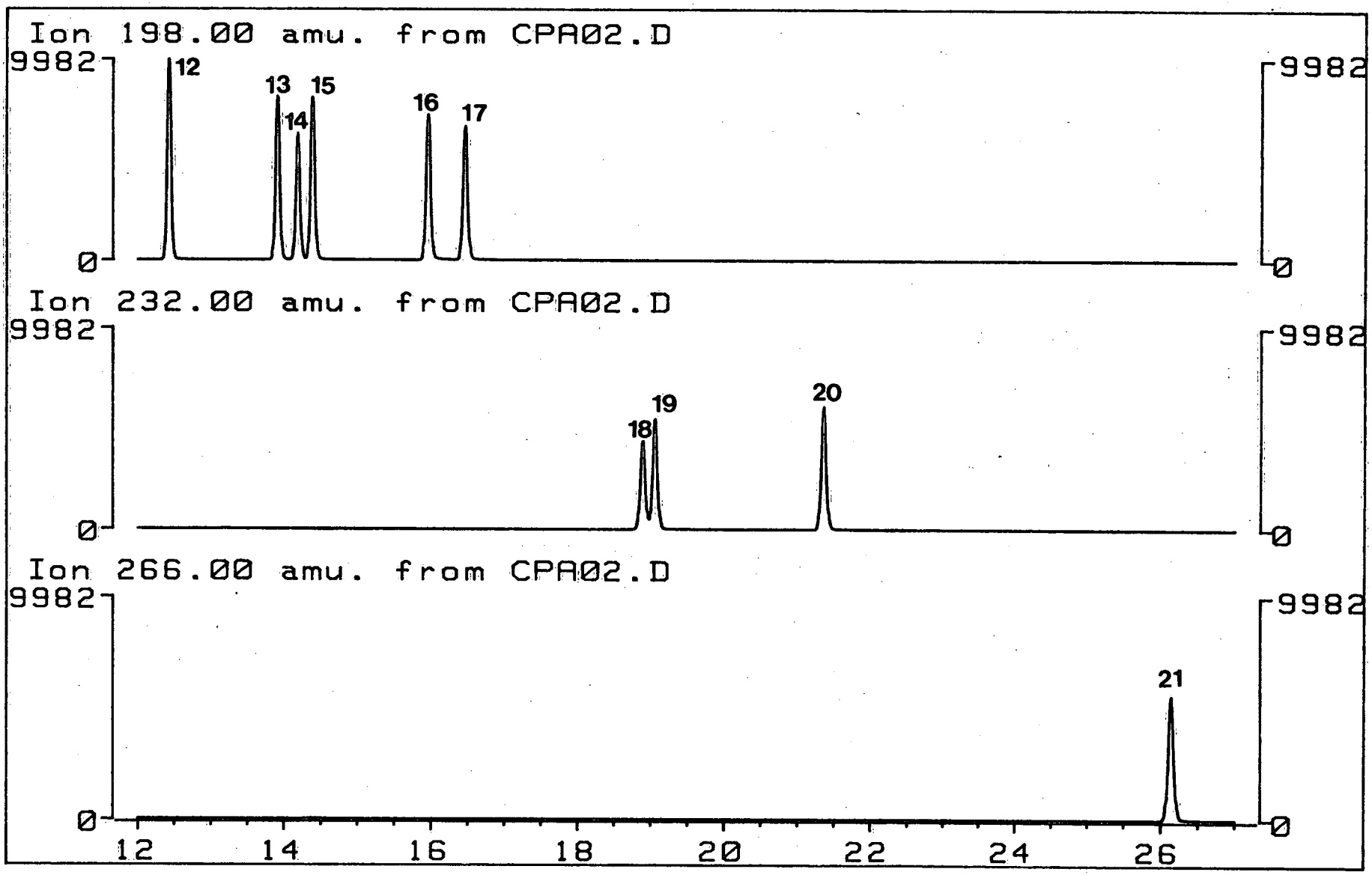
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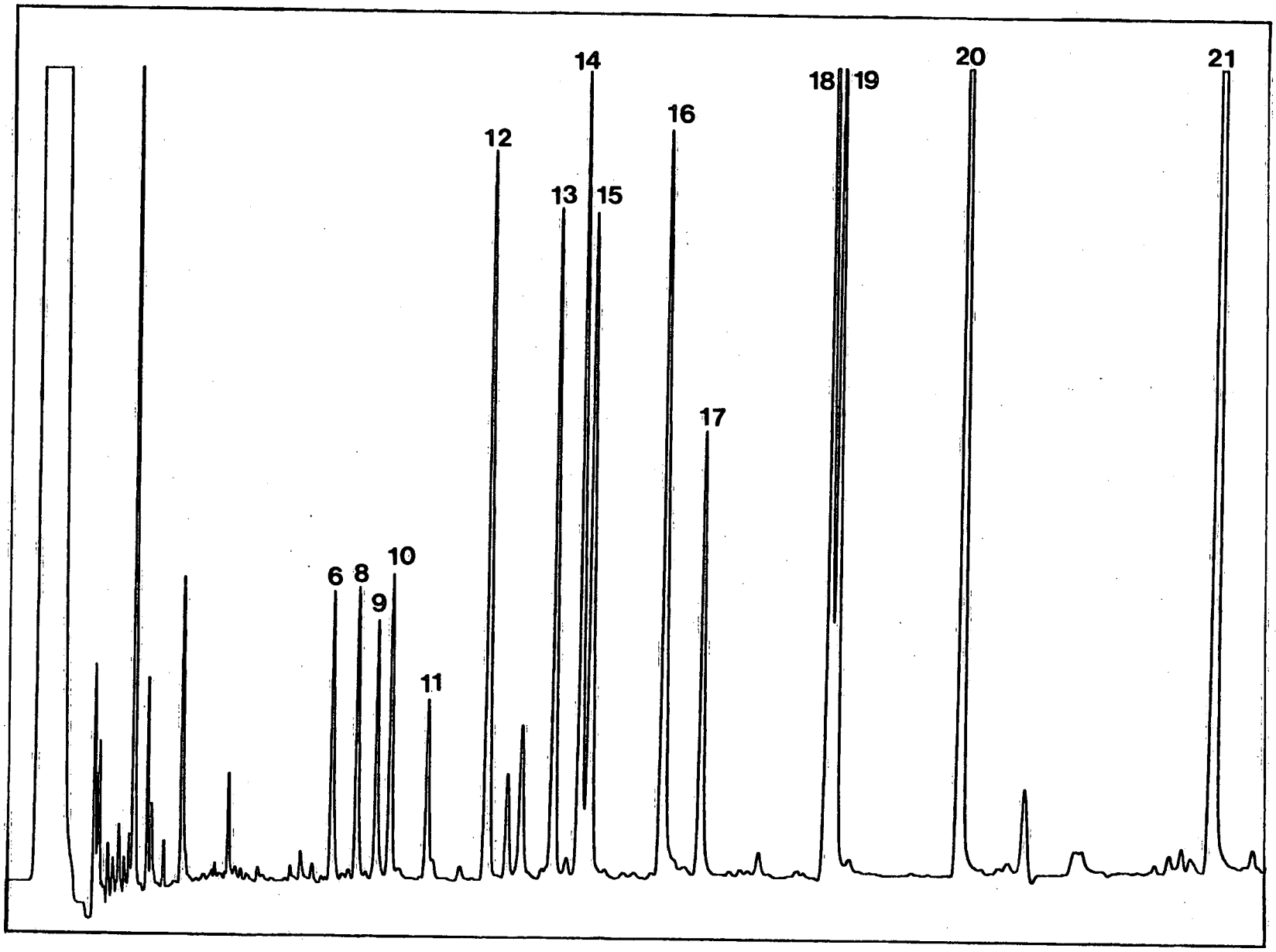
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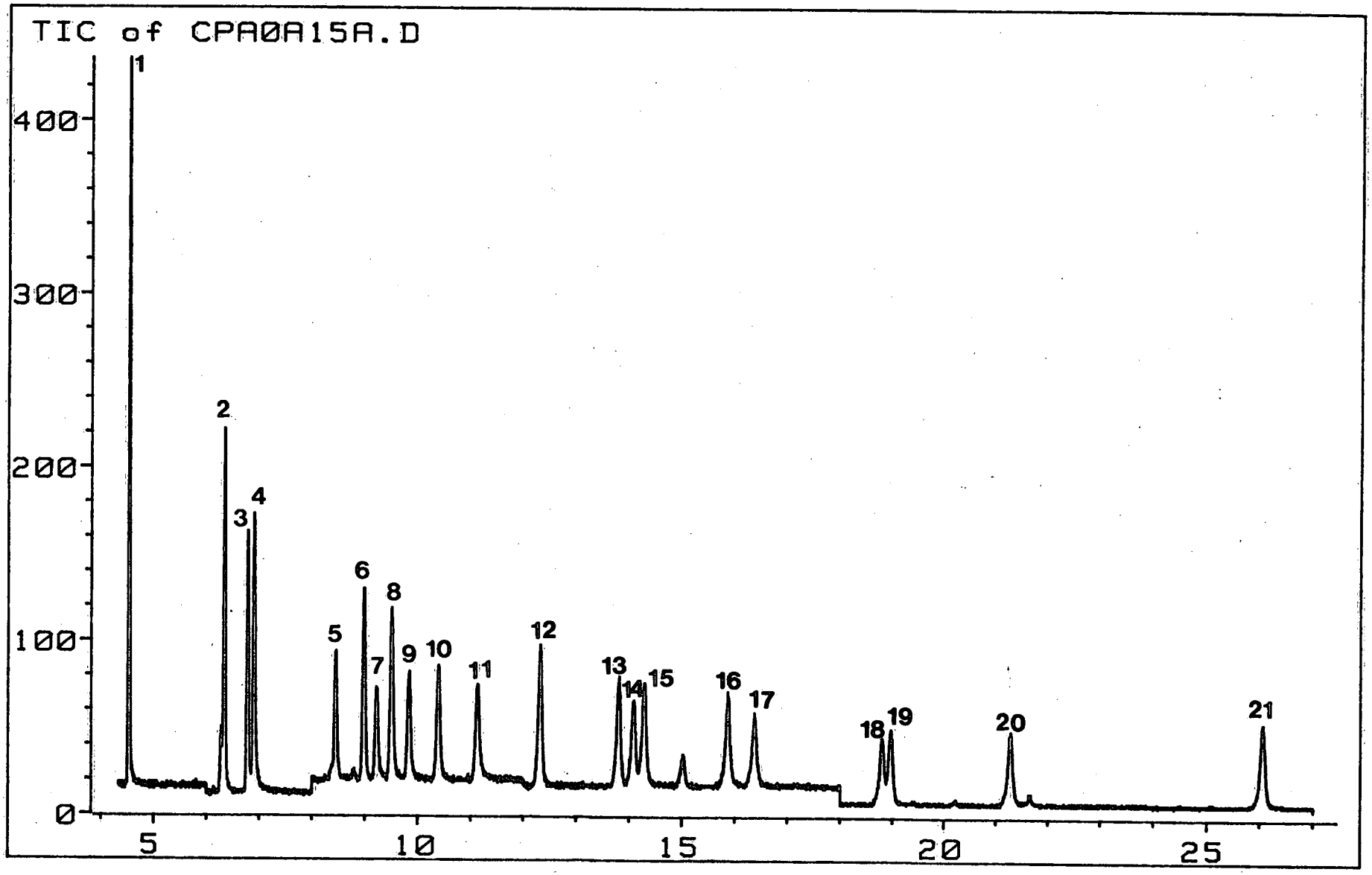
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