Monsanto INDUSTRIAL CHEMICALS COMPANY

R. E. Keller - T1B

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AROCLOR 1016 - ASTM METHODS

PGP 12/17/71 Memo to REK

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B2SH

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The attached method, 71-11A, should be suitable as written for measurement of penta and hexa isomers in Aroclor 1016 for specification purposes. Drs. Munch and Emery recommend that this procedure be submitted to ASTM Committee D-27. This write-up entitled "Gas Chromatographic Determination of Penta- and Hexa-Chlorobiphenyls in Aroclor 1016 and Aroclor 1242" was prepared for distribution outside Monsanto.

We have no method suitable for setting a strict limit against the highly toxic polychlorodibenzofurans in foreign PCB materials. The attached method, 70-23, entitled "Determination of Chlorinated Dibenzofurans in Aroclor Products" has been used in our laboratories by Drs. Dietrich and Mieure to identify and to make a rough estimate of dibenzofurans. It could be rewritten as an identification procedure only but not as a routine quantitative method. Furthermore, this procedure requires a mass spectrometer to identify chromatographic peaks as dibenzofurans. This will immediately rule out a majority of laboratories who use ASTM methods. Additional research work will be needed to develop the gas chromatography/mass spectrometry technique into a sufficiently accurate method. This will take $2,000+ with a 50/50 chance of success for measurement within ±50% relative in the 0-25 ppm range.

Please advise if you feel that additional effort is justified on either writing up an identification method or researching a quantitative method for the dibenzofurans.

REK

R. E. Keller

db
Attachments

DETERMINATION OF CHLORINATED DIBENZOFURANS IN AROCLOR PRODUCTS

INTRODUCTION

Low levels of polychlorinated dibenzofurans have been indicated in competitive polychlorinated biphenyls (PCB's), but not in Aroclor. Because of the reported high toxicity of polychlorinated dibenzofurans, a study was undertaken to determine if these, or related, compounds exist as impurities in our product.

PRINCIPLE

A direct gas chromatographic determination of these impurities is not possible because of interfering PCB components. However, if the Aroclor is eluted with hexane through a column containing Florisil adsorbant, the PCB can be removed, leaving any polar oxygenated compounds adsorbed on the Florisil. These oxygenated materials can then be eluted by a more polar solvent, such as diethyl ether. A procedure based on these principles is described below. Certain polychlorinated naphthalenes and phenanthrenes or anthracenes are also detected by this procedure.

REAGENTS AND APPARATUS

Hexane - Mallinckrodt Nanograde.

Diethyl Ether - Anhydrous Mallinckrodt reagent grade. Two solutions, one 5% and the other 25% by volume, of ether in hexane, were prepared.

Florisil - Fisher, 60-100 mesh, heated at 130°C for 4 hours and stored in a desiccator.

Sodium Sulfate - Anhydrous Fisher certified A.C.S. grade, heated at 400°C for 1 hour and stored in a desiccator.

Liquid Chromatography Columns - 3.6 cm i.d. X 50 cm long Pyrex with Teflon stopcocks.

Gas Chromatograph - A Hewlett-Packard 5750 with a nickel^{63} electron capture detector. The column is 1/4" X 8' glass, packed with 4% XE-60 on 80-100 mesh H.P. Chromosorb W. The helium flow rate is 60 ml/min, the 90% argon, 10% methane purge flow is 120 ml/min, and the oven temperature is 210°C.

Mass Spectrometer - A Varian MAT CH 4B interfaced with a fritted glass separator to a Hewlett-Packard 5750 gas chromatograph equipped with a flame ionization detector.

Sample Concentrator - 500 ml Kunderna-Danish evaporative concentrator with a 3-ball Snyder column and a 5 ml receiver (Ace Glassware).

EXPERIMENTAL

A. Column Preparation

A small amount of glass wool is placed in the bottom of the column, which is then half filled with hexane. Next, 180g of dry Florisil is poured into the column and allowed to settle. Three grams of sodium sulfate is added to the top and one liter of hexane is allowed to elute through the column at a flow rate of about 10 ml/min. The liquid level must not be allowed to drop below the top of the packing. The column can be stored until ready for use as long as the hexane level is maintained above the packing.

B. Column Separation

An accurately weighed sample of Aroclor, about 0.5g, is dissolved in 20 ml of hexane and poured onto the head of the column. The bulk of the PCB is eluted with 2500 ml of hexane, using a 10 ml/min flow rate. This solution is discarded. Next, 800 ml of 5% diethyl ether is eluted through the column and the eluate discarded. Finally, 800 ml of 25% diethyl ether is eluted. Two successive 400 ml portions are collected, starting as soon as the 25% ether is added. These 400 ml portions are saved for further characterization.

C. Concentration of the Samples

Each 400 ml sample is added to a Kunderna-Danish evaporator. The apparatus is placed in a 90°C water bath and heated until the volume has decreased to about 5 ml. The receiver is disconnected and the solution is further concentrated to 1.0 ml by passing purified nitrogen over the surface. Alternatively, the entire concentration can be carried out by evaporation with nitrogen passed over the liquid surface; this is time consuming and some sample is lost on the container walls.

D. Standardization of the Electron Capture GC

A 1 µℓ aliquot of a 1.15 ηg/µℓ solution of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) in hexane is injected into the GC. The chromatogram is recorded and the height and retention time of the peak is measured. TCDD was used as a standard because of the lack of a suitable polychlorinated dibenzofuran standard.

E. Quantitation

An appropriate aliquot (0.5-5 µℓ) of each concentrated sample solution is injected into the electron capture GC. The chromatogram is recorded and the height and retention time of each peak is noted. The concentration of each species in the Aroclor, expressed as ppm TCDD, is

$$\text{Conc(ppm)} = \frac{1.15}{\text{sample wt(g)}} \times \frac{\text{Peak Height(Unk)}}{\text{Peak Height(TCDD)}} \times \frac{\text{Volume Injected(TCDD)}}{\text{Volume Injected(Unk)}}$$

$$\times \frac{\text{Retention Time (Unk)}}{\text{Retention Time(TCDD)}}$$

F. Identification

Excess solvent is evaporated from the sample so that only about 10 µℓ remains. This entire amount is analyzed as one aliquot by GC/MS using standard techniques. The mass spectra of each Aroclor and likely impurities exhibit prominent molecular ion peaks. The number of chlorine atoms per molecule can be calculated from the isotope ratio of the molecular ion. Components identified in this manner can be related back to the chromatogram used for quantitation. Polychlorinated naphthalenes and phenanthrenes or anthracenes have also been observed. We have not verified the quantitation of this procedure for these polynuclear aromatics.

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12/70 - J. P. Mieure, M. W. Dietrich

Physical Chemistry
Method No. 71-11A
Job No. 1346722

GAS CHROMATOGRAPHIC DETERMINATION OF PENTA- AND HEXA-CHLOROBIPHENYLS IN AROCLOR 1016 AND AROCLOR 1242

PURPOSE OF ANALYSIS

This is a rapid, simplified method to be used to determine the level of high boilers (mainly pentachlorobiphenyls) in Aroclor 1016 or similar products. It is not intended for general analysis of chlorinated biphenyl mixtures.

CHROMATOGRAPHIC CONDITIONS

Instrument: Perkin-Elmer 800, Hewlett-Packard 7624A or Equivalent

Type Detector: Flame Ionization

Column: 50' x 0.02" I.D. FFAP S.C.O.T. (Support-Coated Open Tubular) Capillary (Perkin-Elmer Part No. 008-0804)

Column Temperature: 220°C

Detector Block Temperature: 300°C

Injection Port Temperature: 320°C

Sample Volume Injected: 0.005 ml
Split 25 to 1

Flow Rates

Column Helium: 8 ml/min (7 PSIG)
Inlet Splitter: 210 ml/min
Auxiliary or Make-up Helium: 50 ml/min
Hydrogen: 50 ml/min
Air: 400 ml/min

RETENTION TIMES (UNCORRECTED) OF COMPONENTS SEPARATED (CHROMATOGRAMS ATTACHED)

Biphenyl, Mono-, Di-, Tri- and Most Tetra-Chlorobiphenyls (1.0 to 5.0 min); High Boilers (Mostly Penta- and Hexa-Chlorobiphenyls) (5.5 to 11.2 min).

CALCULATION TECHNIQUE

Peak area normalization. The lack of pure knowns prevents the accurate determination of response factors (area correction factors) for the individual components. Therefore, the specification for Aroclor 1016 is simply based on area percent of total high boilers.

PRECISION

Reference samples* of Aroclor 1016 (Drum 2) and Aroclor 1242 (Lot KK 491) were analyzed in duplicate on the two instruments listed using both the Disc chart integrator and an electronic integrator (Infotronics CRS-100 on the Perkin-Elmer 800 chromatograph and Hewlett-Packard 3370A on the Hewlett-Packard 7624A chromatograph). The same column was used in both instruments. Results reported as Area % High Boilers:

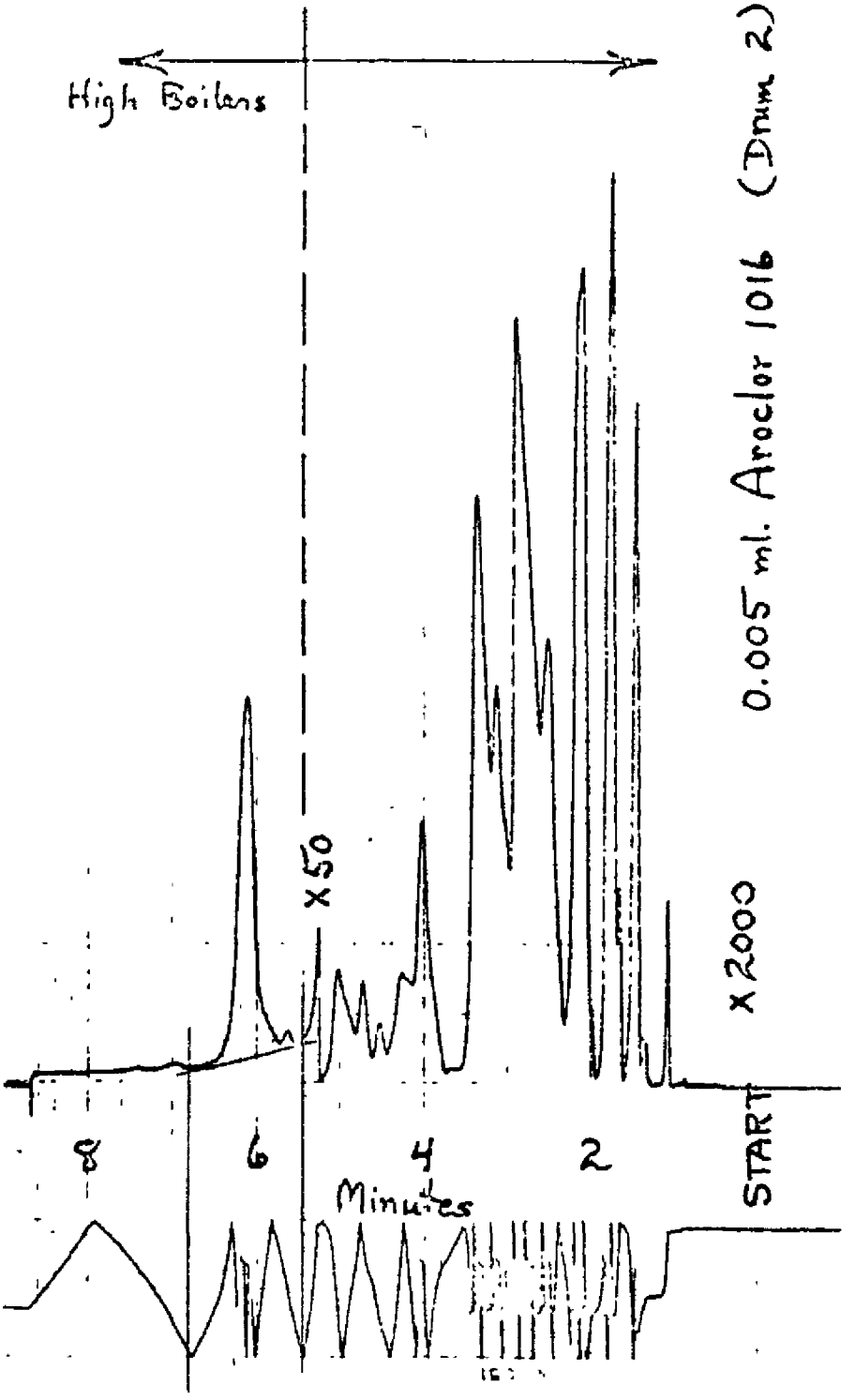
Aroclor 1016 (Drum 2):	Method of Integration		
Chromatograph	Disc Chart	Infotronics CRS-100	Hewlett-Packard 3370A
Perkin-Elmer 800	0.30, 0.27	0.23, 0.21	-
Hewlett-Packard 7624A	0.30, 0.30	-	0.27, 0.28
Aroclor 1242 (Lot KK 491):			
Perkin-Elmer 800	5.88, 5.78	6.22, 5.94	-
Hewlett-Packard 7624A	6.14, 6.32	-	6.63, 6.50

*Portions of these samples are available to laboratories that are setting up this method for control of Aroclor 1016 manufacture.

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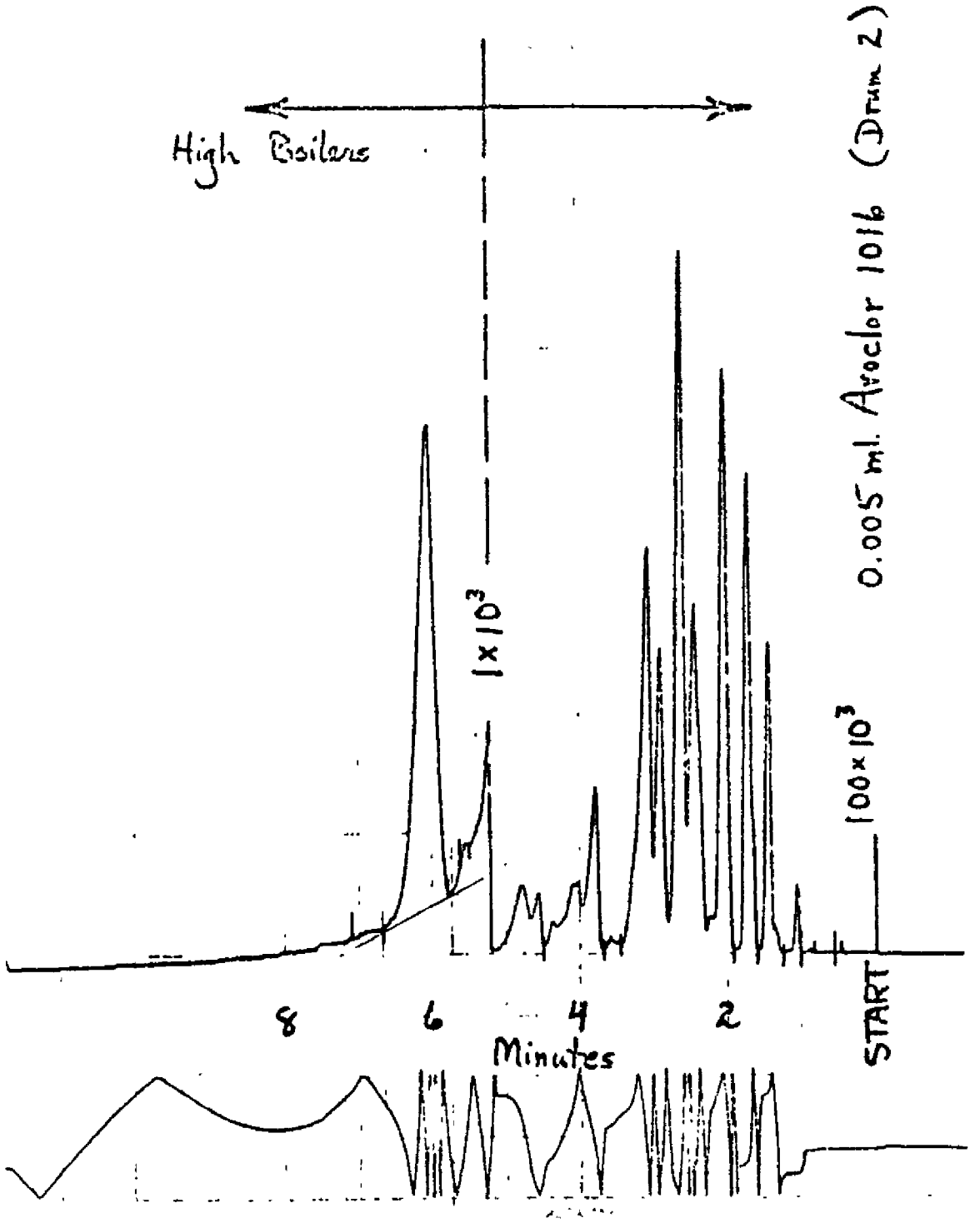
10/71 - G. M. Gasser, E. M. Emery

Perkin-Elmer 800

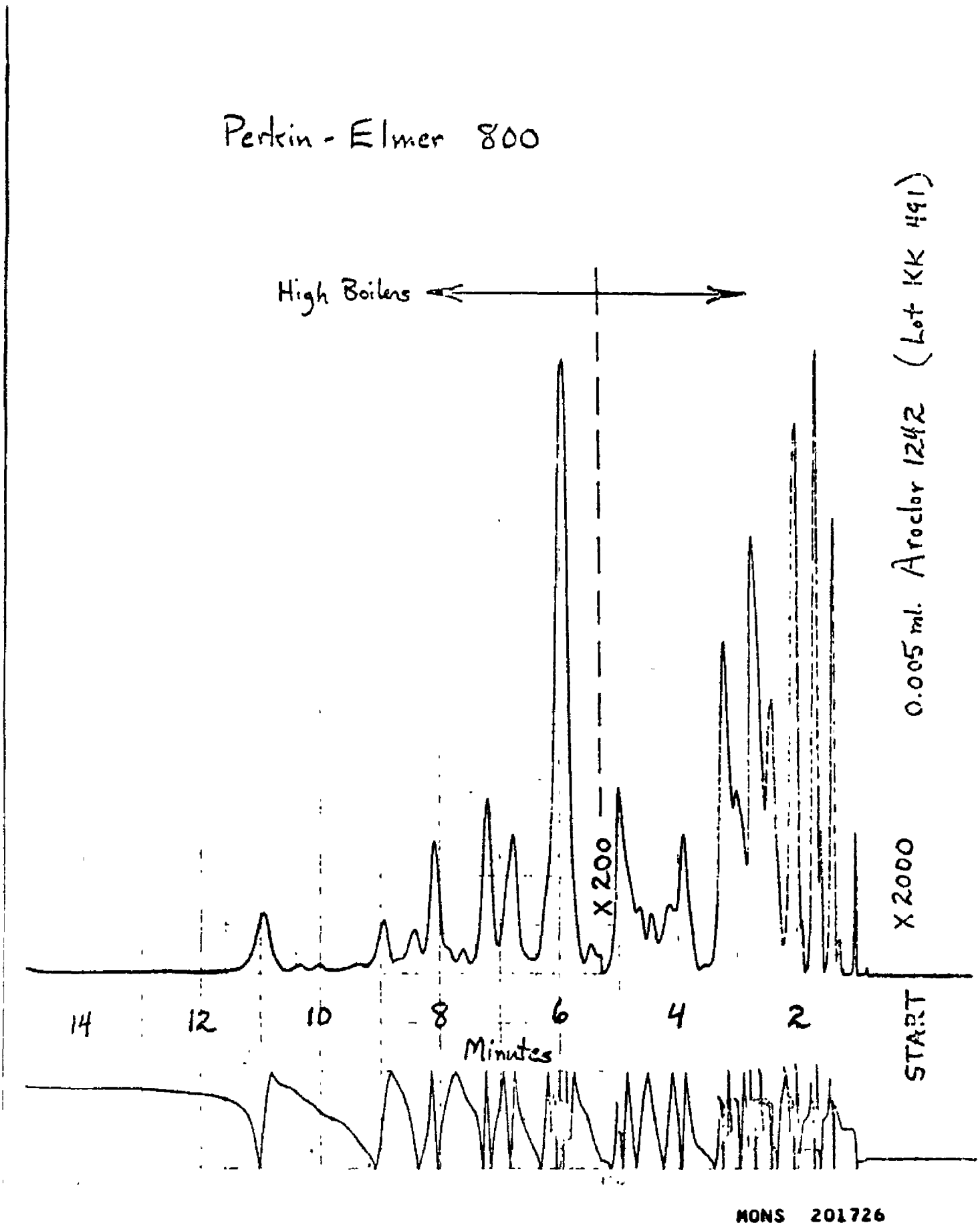


MONS 201724

Hewlett-Packard 7624A

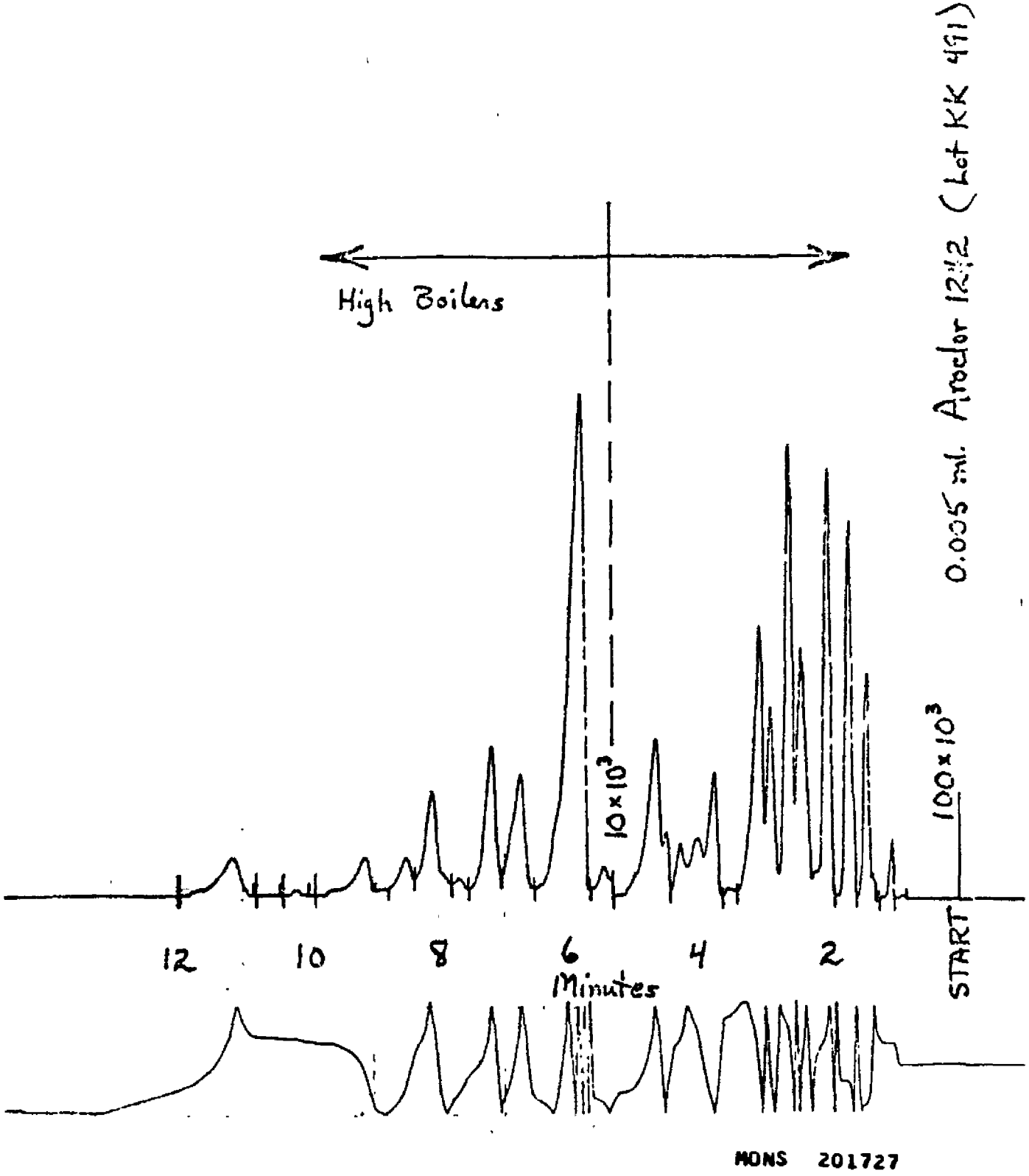


MONS 201725


Perkin - Elmer 800
High Boilers
0.005 ml. Aroclor 1242 (Lot KK 491)
X 200
X 2000
14
12
10
8
6
4
2
Minutes
START

MONS 201726

Hewlett-Packard 7624A



MONS 201727