Monsanto INDUSTRIAL CHEMICALS COMPANY

Aroclor ASTM Methods

FROM (NAME & LOCATION) E. M. Emery - T3E

DATE : November 7, 1972

SUBJECT : PCB PROCEDURES ASTM

REFERENCE :

TO : P. G. Benignus (4)
B2SC

cc: R. E. Keller - T1B
R. H. Munch - T1B
W. R. Richard - T3A
C. Paton - B2SC
W. B. Papageorge - B2NK
T. L. Gossage - B2SL
E. S. Tucker - T2F
M. W. Dietrich - T2B

This is in answer to the comments submitted by Dow Corning on the proposed method for "Gas Chromatographic Determination of Higher Boiling Homologs in ASTM D2233 Type D and Type A (Aroclor 1016 and Aroclor 1242)". As you recall I wrote the original draft of this procedure for Earl L. Morrison. I have not seen the final draft that he submitted to Dow Corning. A copy of my original draft is attached for reference along with a copy of the Dow Corning comments.

I certainly agree with all of the comments made by Dow Corning as representing a more scientific approach to this analysis. We would have preferred using this more scientific approach in our work. However, several difficulties described below have caused us to adopt the simpler empirical approach.

As a former chairman of ASTM Committee E-19 on Chromatography, I am quite familiar with ASTM E 355-68 and E 260-69 referred to by Dow Corning. These two procedures were developed by Committee E-19.

Comment 1 - related to division of the chromatogram

I agree that the retention index is the preferred retention parameter. We chose the simpler approach of providing reference samples with corresponding chromatograms to any laboratory attempting to setup the procedure. The separation will only work properly if the column and total chromatographic system are in good condition and operated properly. We felt that another laboratory could most easily tell if they were properly carrying out the analysis by running sequence samples.

It may well be that ASTM will not allow the use of reference samples. In that case certainly the use of retention indices to describe the division of the chromatogram and the range over which the compounds are measured is the best approach.

ASTM Committee E-19 has been recently studying the reproducibility of retention indices between laboratories which were all supplied the same batch of column packing. We found a surprising variability in the reported retention indices. The retention index is of course temperature dependent. It was felt that this variability was due to the fact that the thermocouple/pyrometer readout systems on most commercial chromatographs are quite inaccurate. Certainly if retention indices are to be used in this procedure, then it will be necessary to specify that the column temperature be measured by some more accurate means.

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Comment 2 - on use of pure known calibration materials

We have found by GC/MS that even when we slow the analysis down using a longer column, there is still overlap of the tetra- and penta-chlorobiphenyls. In addition, most of the peaks contain more than one component (sometimes of differring chlorine level) and the ratio of these components in some peaks can vary depending upon the source and method of manufacture of the Aroclor 1242. Therefore, to apply individual response factors even in the case where one has pure known compounds would require a GC/MS run on each sample being analyzed. We felt that this was not practical for the majority of laboratories. Therefore we have adopted the more rapid empirical procedure for plant control use, recognizing that it does not give the true absolute level of penta- and hexa-chlorobiphenyls.

Comment 3 - on sensitivity and minimum detectable amounts

I agree and such information can be obtained experimentally if the need for it is accepted.

Comment 4 - on precision

This relates to something that must have been added to a later draft. Five measurements would certainly give better precision than two, but of course only in the ratio of the square roots of the number of measurements.

I am sending along extra copies of this memo that can be forwarded to Dow Corning and other interested parties.

E. M. Emery

att.

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GAS CHROMATOGRAPHIC DETERMINATION OF HIGHER BOILING HOMOLOGUES IN AROCLOR 1016 AND AROCLOR 1242[1]

1. SCOPE

1.1 This is a rapid procedure to be used to determine the level of higher boiling homologues in Aroclor 1016 and Aroclor 1242. It is not for use on other Aroclor products and is not intended for general analysis of polychlorinated biphenyl mixtures.

2. SUMMARY OF METHOD

2.1 The sample is injected into a support-coated open tubular gas chromatography column. The components are separated as they pass through the column with helium carrier gas and their presence in the effluent is measured by a flame ionization detector and recorded on a chromatogram. The method is made quantitative by internal normalization comparing the area of the higher boiling homologue peaks to the total area of all the peaks in the chromatogram.

Note 1 - Reference should be made to ASTM Method E260, General Gas Chromatography Procedures and ASTM Method E355, Gas Chromatography Terms and Relationships[2].

2.2 This method arbitrarily splits up the chromatogram into two regions. The major region represents mostly mono, di, tri and tetra-chlorobiphenyls. The lesser region represents the higher boiling homologues and is mostly penta and hexa-chlorobiphenyls. However, there is some overlap of the tetra and penta-chlorobiphenyls between the two regions. Some of the important peaks in the major region contain both tetra and penta-chlorobiphenyls.

The only way to obtain a closer approximation to true composition of these samples is to use a longer column with a gas chromatography/mass spectrometry combination to correct for the composition of these overlap peaks. Area correction factors must also be used. However, GC/MS instrumentation is not available in many laboratories and is too cumbersome and costly for routine analysis. Therefore, this empirical short method has been adopted.

3. APPARATUS

3.1 Chromatograph - Any gas chromatograph with flame ionization detector and capillary column inlet splitter system.

3.2 Recorder - 0 to 1 or 10 mV range with full-scale response time of 1 sec. and chart speed of approximately 1/2 inch/min.

(1) This method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases.

(2) Annual Book of ASTM Standards, Part 30.

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3. APPARATUS (Cont'd)

3.3 Column - Fifty foot by 0.02 inch I.D. support-coated open tubular (S.C.O.T.) capillary coated with FFAP available from Perkin-Elmer Corporation as Part No. 008-0804.

3.4 Integrator - Disc chart integrator or electronic digital integrator to measure the peak areas. If an electronic integrator is used, it should be checked initially against a Disc chart integrator to determine that the electronic integrator operating parameters have been set properly for correctly measuring the late eluting small peaks.

4. INSTRUMENT PARAMETERS

4.1 Column - 50' X 0.02" I.D. Support-coated open tubular capillary coated with FFAP (Perkin-Elmer Part No. 008-0804).

4.2 Temperatures -

Column: 220°C (isothermal)
Sample Inlet System: 320°C
Detector: 300°C

4.3 Gas Flow Rates -

Column: 8 ml/min. (7 PSIG) helium
Inlet Splitter: 210 ml/min. helium
Auxiliary or Make-Up: 50 ml/min. helium
Hydrogen: Note 3
Air: Note 3

Note 3 - Adjust air-hydrogen ratio to give maximum detector sensitivity. See the Instrument Instruction Manual.

4.4 Sample Size - 0.005 ml split 1 to 25.

5. CALIBRATION

5.1 The method of calculation is peak area normalization. The lack of pure knowns prevents the accurate determination of response factors (area correction factors) for the individual components. Therefore, the results are reported as area per cent of total high boilers.

6. PROCEDURE

6.1 Adjust the chromatograph to the above conditions.

6.2 Inject 10 µℓ of the neat sample and allow the chromatogram to proceed at attenuation settings which will keep all the peaks on the scale if the Disc chart integrator is being used.

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6. PROCEDURE (Cont'd)

6.3 Final check-out of the total chromatographic system for this analysis can best be done using the reference samples of Aroclor 1016 and Aroclor 1242 referred to in the Precision Section.

Portions of these two reference samples are available from Dr. E. M. Emery, Monsanto Company, Mail Zone T3E, 800 N. Lindbergh Blvd., St. Louis, Missouri 63166.

7. CALCULATION

7.1 Divide the chromatogram into two regions as shown on the accompanying chromatograms.

7.2 Measure the total area of the peaks in each region of the chromatogram.

7.3 Calculate the result as follows:

$$\text{Area \% Higher Boiling Homologues} = \frac{\text{Area of High Boilers}}{\text{Total Area of All Peaks}} \times 100$$

8. PRECISION

8.1 Reference samples of Aroclor 1016 (Drum 2) and Aroclor 1242 (Lot KK 491) were analyzed in duplicate on two different instruments using both the Disc chart integrator and an electronic integrator. An Infotronics Model CRS-100 integrator was used on a Perkin-Elmer Model 800 chromatograph and a Hewlett-Packard Model 3370A integrator was used on a Hewlett-Packard Model 7624A chromatograph. The same column was used in both instruments.

8.2 Results are given below in Area % High Boilers:

MCS 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

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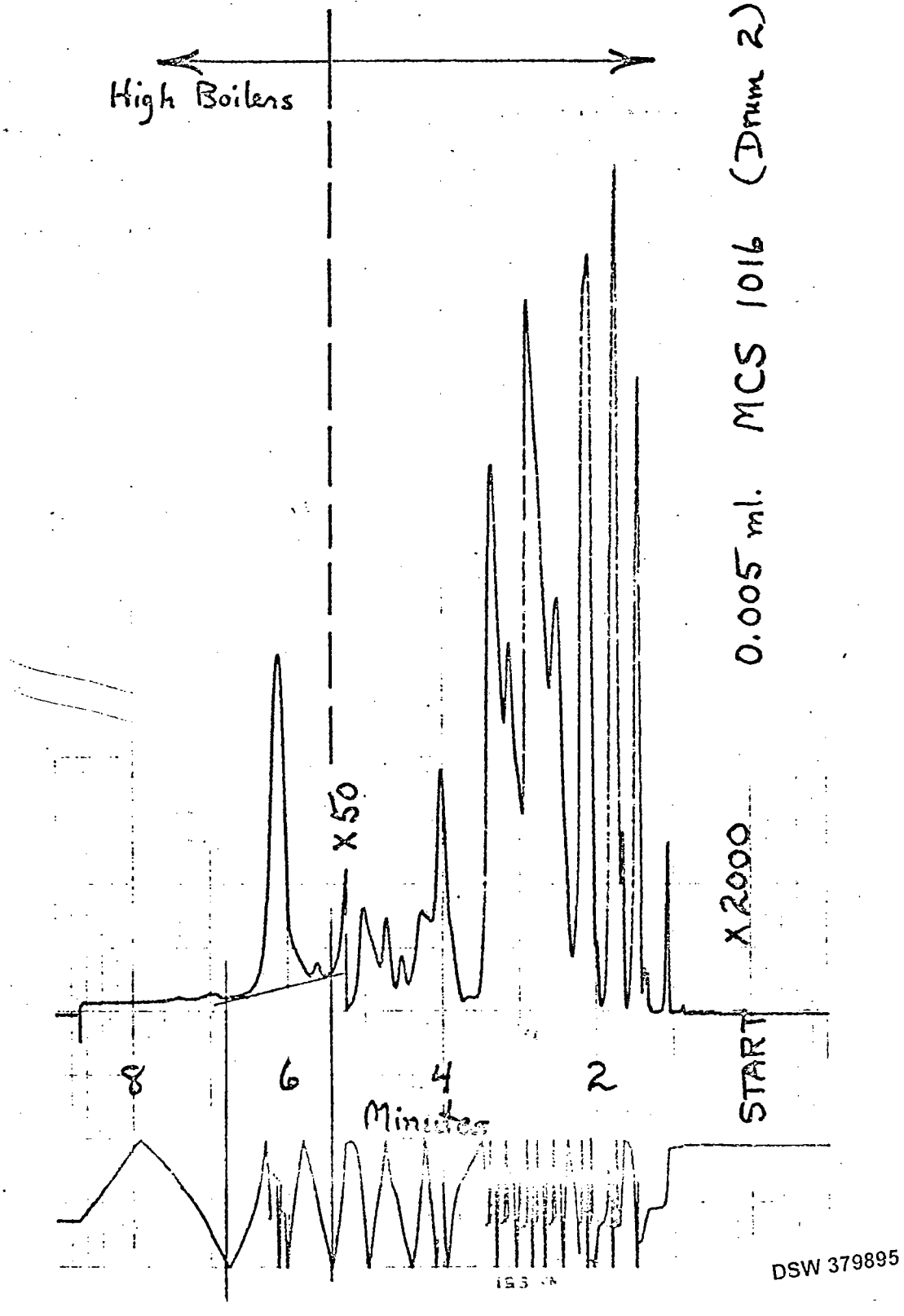
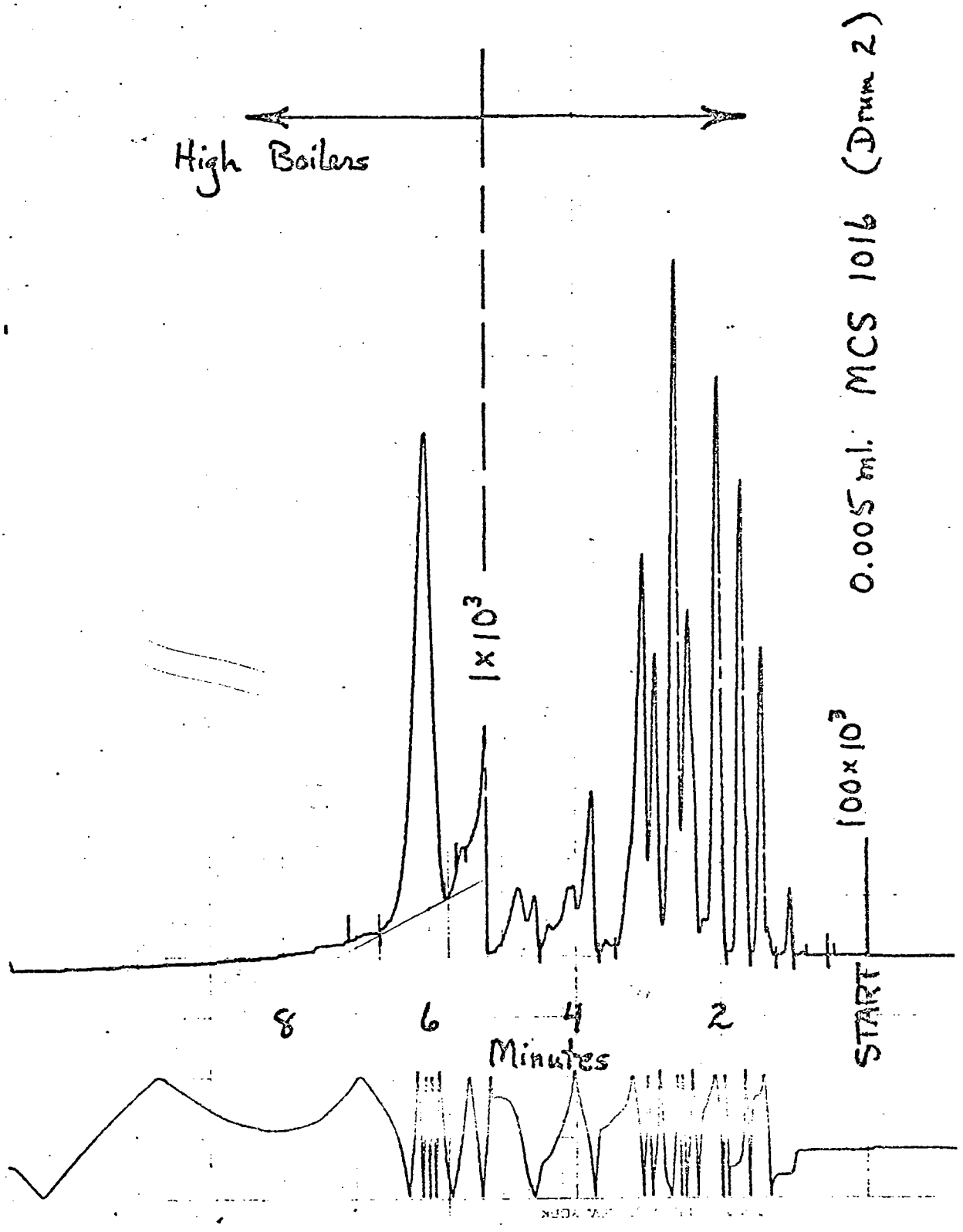
Perkin-Elmer 800



Hewlett-Packard 7624A



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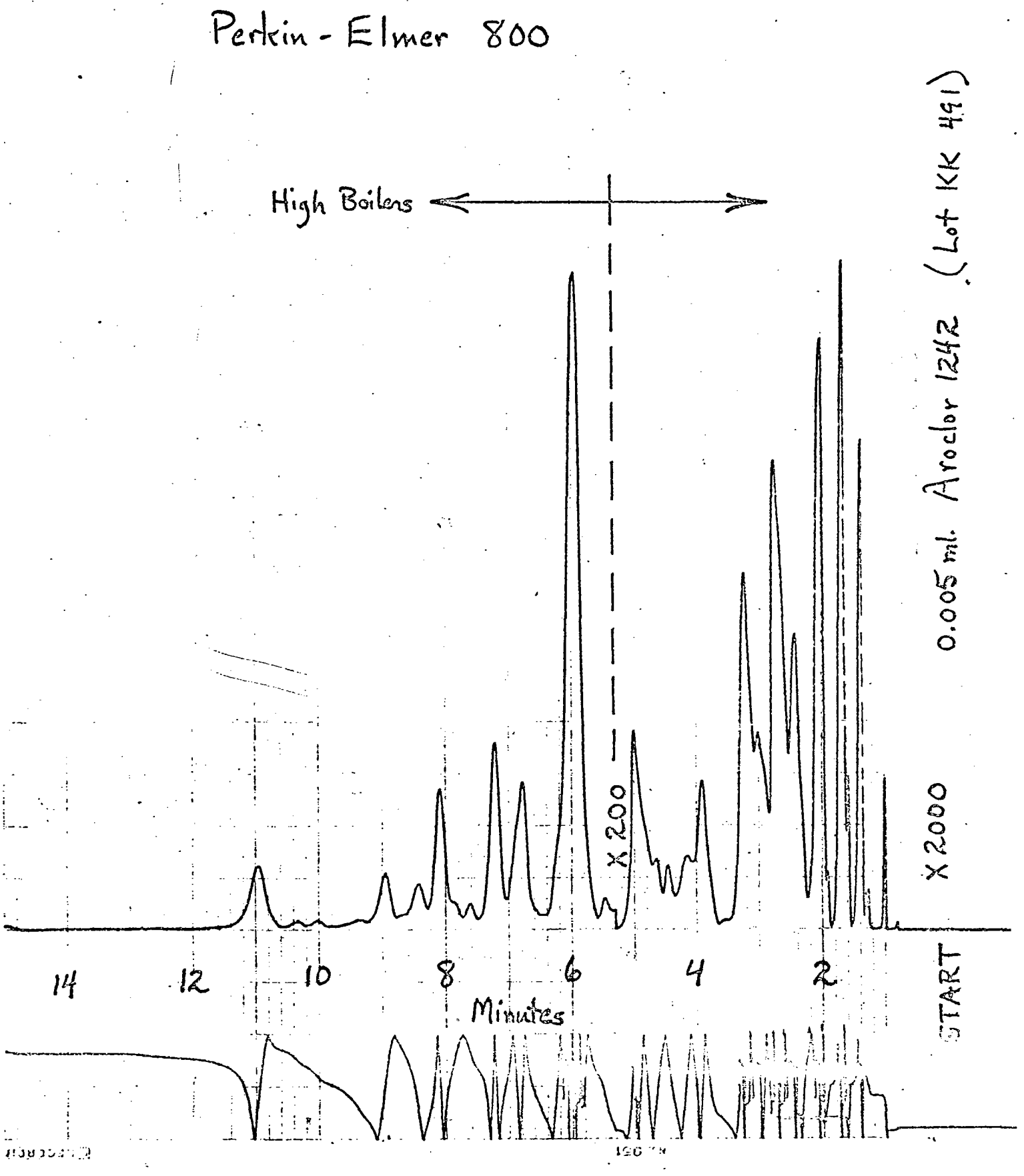

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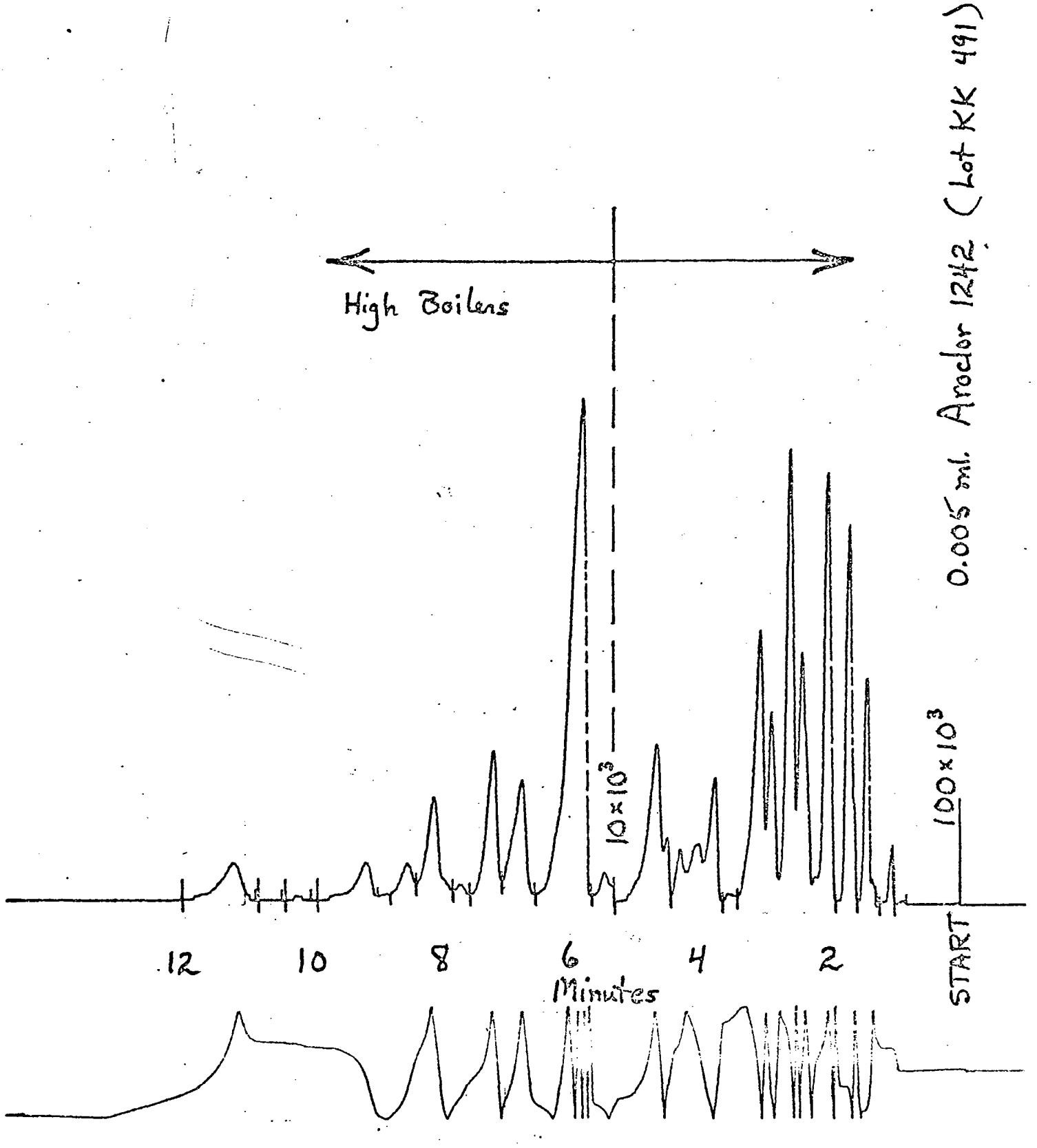
Hewlett-Packard 7624A



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COMMENTS ON PCB METHODS

Method I. Gas Chromatographic Determination of Higher Boiling Homologues in Aroclor 1016 and Aroclor 1242.

1. There should be a clearer definition of how the chromatogram is divided and over what range the elution is recorded.

   Recommendations:

   a) Describe the division of the chromatogram in terms of a retention index (ASTM's preferred retention parameter E 355-68, p. 1128); e.g., all components eluting with a retention index greater than 2400 will be calculated as a "High Boiler."

   b) In a similar manner the range over which compounds are measured could be described using a retention index window: e.g., all compounds eluting with retention index 100 $<I_x<2400$ are "Low Boilers," those with $2400 <I_x <3600$ are "High Boilers."

2. Although pure known materials are generally not available, Dr. Ronald G. Webb, Southeast Environmental Research Laboratory, National Environmental Research Center - Corvallis, Environmental Protection Agency, Athens, Georgia 30601 can provide samples of materials whose compositions have been determined by a combination of elemental analysis, gas chromatography with a Coulson conductivity detector and combined gas chromatography - mass spectrometry. Using these as standards, response factors can readily be determined.

3. The method should provide information on sensitivity and minimum detectable amounts. Refer to ASTM E260-69, p. 748.

4. For precision, five rather than two measurements should be made.

Method II. Polychlorinated Biphenyls in Petrochemicals.

1. In Note 1, there appears to be some confusion of the terms "sensitivity" and "minimum detectable limit."

2. Method Summary:

   a) Is documentation available to show that compounds elute in boiling point order? It is generally accepted that the free energy of solution determines elution order in gas-liquid partition chromatography, rather than the boiling points.

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b) Many hydrocarbons with functional groups show strong electron capture response.

3. It seems that 100 µl is an awfully large sample to inject on to a 3.5% loaded column. That much material would probably kill the response of a Ni^{63} electron capture cell.

4. Retention parameters should probably be expressed in terms of retention indices. Refer to ASTM E 355-68.

5. Provide some information on precision, accuracy, and sensitivity measurements as per ASTM E 260-69.

6. We have found that PCBs are adsorbed readily on untreated glass surfaces. Serial dilutions should not be made in glass containers unless the glass is properly pre-treated.

R. T. Bruce
Don Corning

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