WGK 148

MONSANTO CHEMICAL COMPANY
W. G. KRUMMRICH PLANT LABORATORY

# STANDARD ANALYTICAL METHOD

| DATE ISSUED | PAGE | NUMBER |
|---|---|---|
| 8/4/72 | 1 OF 5 | 13,268 |
| WRITTEN BY: JHFrancis | APPROVED BY: HJHorner | |
| ATTACHMENTS: Sample Chromatograms (3) | | |

PRODUCT: MCS1016, 1242 Aroclor, Monochlorobiphenyl (Crude and Finished Goods)

TEST: Higher Boiling Homologs

THIS FORM ☐ SUPERSEDES METHOD _____ ISSUED ON 7/20/71
☒ REVISES INSTRUCTIONS of 7/20/71. T-2302

## SCOPE

This procedure determines higher boiling homologs in MCS 1016 and in 1242 Aroclor. Approximate isomer distribution can also be determined on MCS 1016, 1242 Aroclor and monochlorobiphenyls.

DO NOT USE THIS PROCEDURE WITH HIGHER CHLORINATED BIPHENYLS. THEY ELUTE FROM THE GLC COLUMN WITH EXTREME DIFFICULTY AND ONLY AT TEMPERATURES THAT DRASTICALLY SHORTEN COLUMN LIFE.

## EQUIPMENT AND SUPPLIES

1. GLC Instrument, Varian-Aerograph Model 144410-00, flame ionization detector, capillary splitter, linear-programmed, single column. Varian-Aerograph, 2700 Mitchell Drive, Walnut Creek, California 94598 (or equivalent).

2. Recorder, any good 1 mv. full scale, 1-second or less response time equipped with DISC or electronic integration.

3. Column, 50 ft. x 0.02 inch I.D. S.C.O.T. column with FFAP liquid phase. Perkin Elmer Corp., Norwalk, Conn. 06852.

4. Syringe, 0.2 ul fixed-volume, Precision Sampling Co. Cat. No. 200002 (or equivalent syringe to deliver 0.2 ul). Fisher Scientific Co., 1241 Ambassador Blvd., St. Louis, Mo. 63132.

5. Standard samples for calibration are available from E. M. Emery, Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, Mo. 63166.

## SAFETY

Chlorinated biphenyls are now considered environmental contaminants. Handle with care and dispose of waste and spill cleanup in the prescribed containers.

GLC injection ports and ovens are usually very hot. Take care not to touch the hot equipment.

INSTRUMENT CONDITIONS

| | |
|---|---|
| Injection Port | 325 + 10°C |
| Detector | 320°C |
| Column Oven | 235°C Isothermal* |
| Range (input) | 10-11 Amps/MV |
| Column Helium Flow | 10 cc/min. at room temperature |
| Splitter Flow | 50 cc/min (equiv. to a 5-1 split) (12 secs./10 cc) |
| Hydrogen | 30 cc/min (20 sec/10 cc) |
| Air | 300 cc/min (2 secs/10 cc) |
| Injection | 0.2 ul |

* Column temperature may be adjusted downwards as the column ages, to maintain retention time. Different column temperature may be necessary for monochlorobiphenyl isomer distribution.

Normal back-pressure at the injection part is 12-18 psig.

DETERMINATION

1. Bring the instrument to the conditions described above for at least 5 minutes. The baseline should be stable at 4-1 attenuation. Set the attenuator at 256-1 before injecting the sample if Disc integration is to be used. Electronic integration can be at any attenuation but the RANGE setting must not be changed during a run.

2. Load the syringe by immersing the needle at least 1 inch below the surface of the sample and moving the plunger in and out slowly for at least 5 cycles or until the small bubbles of air are no longer expelled from the needle. Wipe the needle off with a soft tissue.

3. Depress the computer start button to activate the computer scan and immediately inject the sample into the GLC. Leave the needle in the injection port for 5-6 seconds and then withdraw slowly.

4. If Disc integration is used the attenuation must be changed to 2-1 or 16-1 after 16 minutes (new column) so that the high boilers elute with a large enough peak(s) to integrate accurately (see sample chromatograms).

DETERMINATION (Cont'd.)

5. The chromatogram should be complete in 20 minutes for MCS 1016 and in 30 minutes for 1242 Aroclor. Monochlorobiphenyls should be complete in less than 20 minutes. (If the computer program is used it will automatically end at 30 minutes for all samples.)

6. Determine the counts under the MCS 1016 peak envelope (1-16 minutes) and for the combined higher boiling Homologs (16-30 minutes).

CALCULATION

$$\% \text{ Higher Boiling Homologs} = \frac{\text{Area for High Boilers} \times 100}{\text{Total Area}}$$

$$\% \text{ Isomer (individual)} = \frac{\text{Area for Isomer} \times 100 \times \text{ACF}^*}{\text{Total Area (Corrected)}}$$

* Monochlorobiphenyls will require area correction factor for BiØ. See sample curve.

Report the results to the nearest 0.01%.

Duplicate analyses are expected to check to within 0.04% (actual).

Precision data should be collected as soon as is feasible.

DISCUSSION

According to recent information pentachlorobiphenyls and higher chlorinated isomers are very difficult to biologically degrade and tend to concentrate in fish and birds. This test is being performed to help keep these isomers to a minimum in MCS 1016.

This procedure was adapted from Method No. 71-11, Job No. 1348522, Physical Chemistry Dept. The procedure compares Disc and electronic integration and results are comparable and within expected tolerances.

DISCUSSION (Cont'd.)

Apparently different S.C.O.T. columns vary considerably. W.G.K. columns at the same conditions as those specified in Method No. 71-11 give considerably longer retention times and improved separation with less tailing.

Column life is expected to be about 1 month at 235°C. Column life can be extended if when there are to be no samples for several hours the column temperature is reduced to 150°C. It should only take about 30 minutes for the column to restabilize when the temperature is again increased to 235°C. A spent column will be indicated when the peaks show marked tailing and loss of separation of some of the doublet peaks. If in doubt refer to the sample chromatograms.

Monochlorobiphenyl is a relatively new product and standards are not presently available to prepare a sample chromatogram. It is expected that the column temperature will have to be reduced to about 200°C to effect a proper separation of the isomers. Order of elution of components will be Biphenyl, o-Chlorobiphenyl, m-chlorobiphenyl, p-chlorobiphenyl, then dichlorobiphenyls and trichlorophenyls. Higher chlorinated isomers are not expected to be present.

We expect production to eventually ask for analysis of Recovered Biphenyl for chlorobiphenyls. The Recovered Biphenyl will probably be a solid at room temperature. Dilution in benzene (1-1 volume/volume) and injection of 0.5 ul should handle this type sample. (Benzene counts would then be ignored in the area normalization.) A 1 ul syringe with the plunger in the needle should be used for this injection.

Hydrogen and air flows can be checked by attaching a bubble meter to the flow diverters on the right side of the instrument and pushing in all the way. When finished checking the flows make sure the diverters are pulled all the way out and then re-ignite the flame detector. Column flow is checked by disconnecting the column exit end and checking the flow with a bubble meter. Splitter flow is checked at

DISCUSSION (Cont'd.)

the split exit on the right side of the instrument. These flows should be checked at least once a week or whenever abnormal operation is suspected. Occasionally the flame becomes extinguished for unknown reasons. If after an injection has been made and peaks are overdue or extremely small check to see if the flame is still lit by holding in the igniter button for about 5 seconds. The cap on the detector will usually "pop" if the flame was out. The injection must then finish eluting before an analysis can be restarted.

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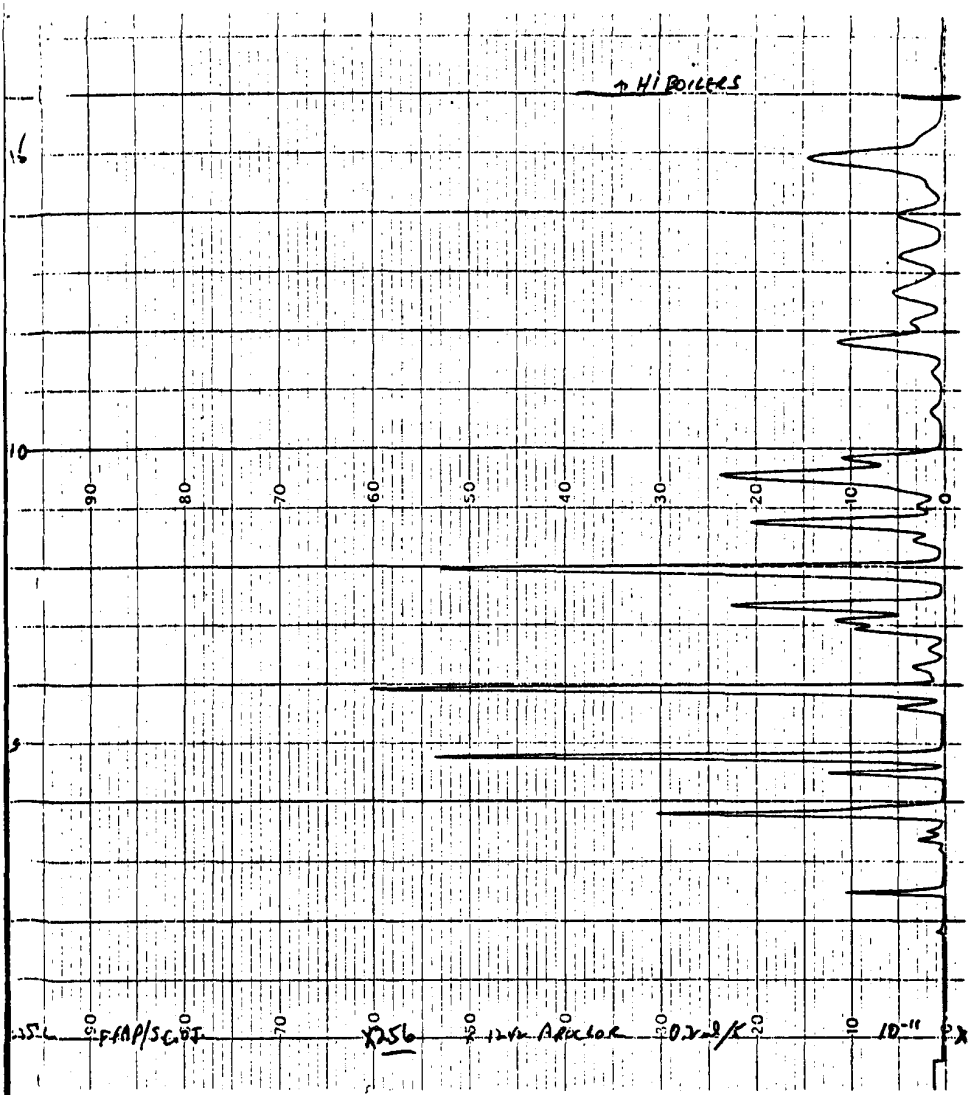


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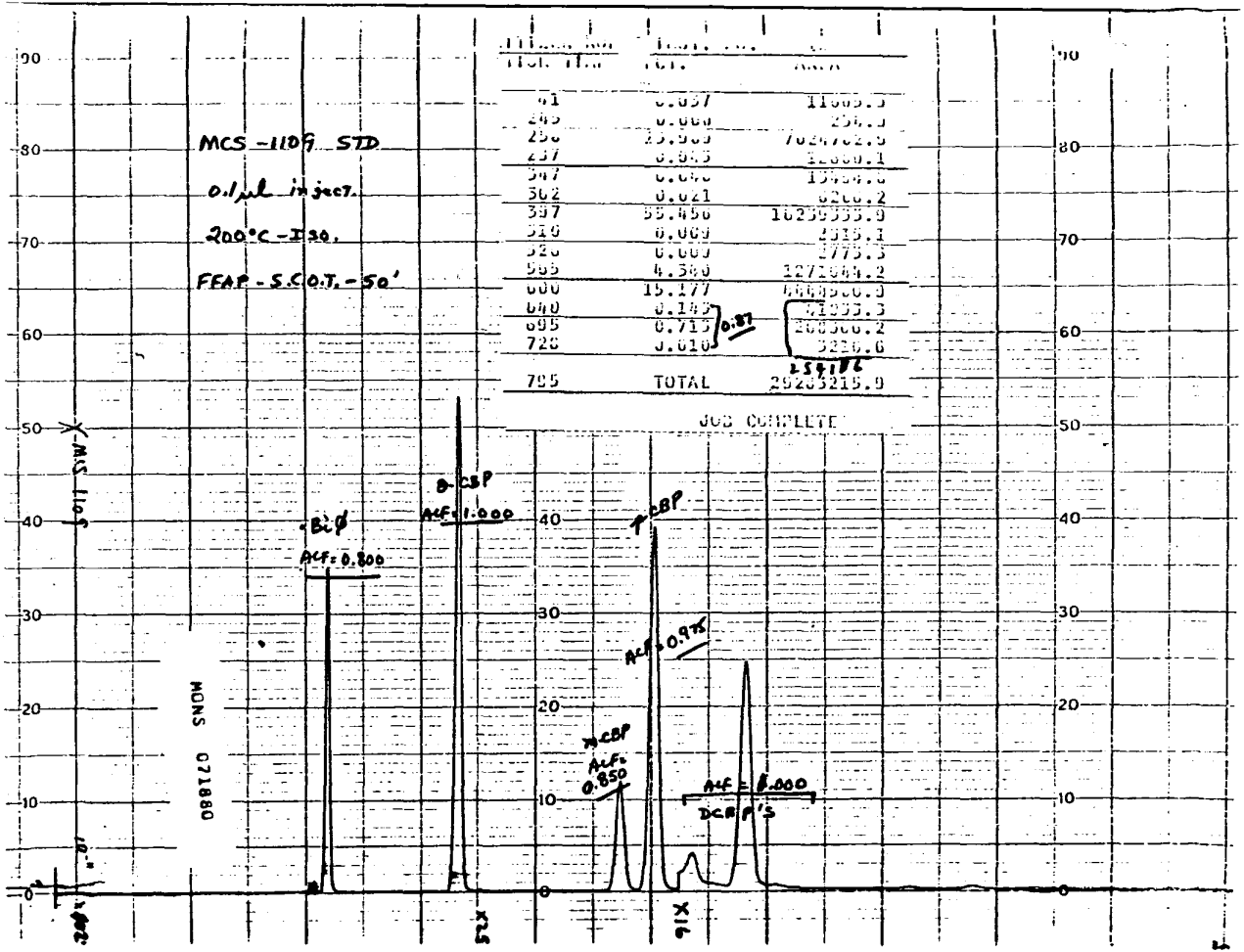


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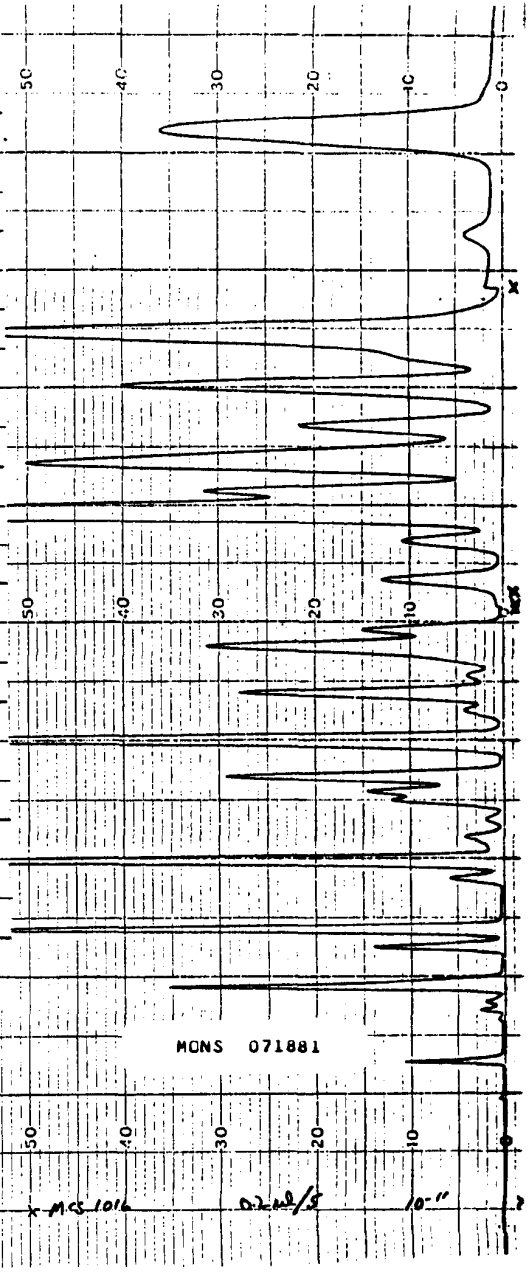
|---|---|---|
| 41 | 0.037 | 11605.3 |
| 245 | 0.000 | 254.3 |
| 256 | 23.969 | 7024702.5 |
| 237 | 0.043 | 12860.1 |
| 347 | 0.046 | 13454.6 |
| 362 | 0.021 | 6266.2 |
| 397 | 55.456 | 16239333.9 |
| 310 | 0.009 | 2315.1 |
| 326 | 0.009 | 2775.3 |
| 565 | 4.340 | 1271644.2 |
| 600 | 15.177 | 4444560.9 |
| 640 | 0.145 | 41933.3 |
| 695 | 0.715 | 208366.2 |
| 728 | 0.010 | 3216.6 |
| 795 | TOTAL | 29283215.9 |

JOB COMPLETE

| [illegible] TIME | PCT. | AREA |
|---|---|---|
| 30 | 0.001 | 488.0 |
| 38 | 0.005 | 2558.0 |
| 63 | 0.001 | 711.0 |
| 94 | 0.000 | 344.0 |
| 108 | 0.040 | 19494.5 |
| 107 | 0.958 | 466653.0 |
| 132 | 0.047 | 23024.0 |
| 201 | 0.277 | 133596.4 |
| 210 | 0.223 | 107338.0 |
| 224 | 5.464 | 2627203.4 |
| 266 | 1.937 | 931248.4 |
| 283 | 0.960 | 4307814.9 |
| 330 | 0.942 | 452696.3 |
| 353 | 12.681 | 6098636.9 |
| 377 | 0.946 | 456216.6 |
| 395 | 0.325 | 156418.3 |
| 415 | 2.175 | 1046023.3 |
| 424 | 2.782 | 1337673.4 |
| 438 | 6.387 | 3071655.4 |
| 476 | 16.778 | 8066566.9 |
| 507 | 0.921 | 443064.0 |
| 524 | 0.729 | 3235217.9 |
| 542 | 0.855 | 411244.8 |
| 72 | 10.267 | 4935529.9 |
| 69 | 3.414 | 1641715.9 |
| 637 | 0.501 | 240916.3 |
| 678 | 0.396 | 190480.6 |
| 700 | 5.095 | [illegible] |
| 730 | 1.088 | 523286.6 |
| 759 | 2.804 | 1348361.4 |
| 796 | 0.921 | 442698.3 |
| 837 | 1.768 | 850148.3 |
| 865 | 0.333 | 160311.5 |
| 892 | 3.574 | 1718606.5 |
| 934 | 0.012 | 6049.5 |
| 1095 | 0.369 | 177577.5 |
| 1204 | 0.004 | 2018.5 |
| 1331 | 0.000 | 138.0 |
| 1655 | TOTAL | 48675471.9 |

0.38

JOB COMPLETE



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| 2331 | TOTAL | 42692351.9 |

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