

AROCLOR ENVIRONMENTAL PROGRAM

EUROPEAN TRIP - MAY 1-21, 1970

Summary of Analytical Findings

1. No significant advances have been made in methodology in Europe and the UK the past year for the identification and measurement of PCB's. One new approach involves use of thin layer chromatography at Folkhalsan in Sweden prior to gas chromatography to get free of interferences and obtain increased specificity. A technique involving extraction with cold acetone for isolation of PCB's from tissue may shorten our tissue analysis program markedly.

2. No new analytical workers with the exception of Wiggins-Teape in the UK and Folkhalsan in Sweden have become involved in Europe during the past year.

3. Competitive companies in Germany (Bayer), France (Prodelec) and Italy are about where Monsanto was one year ago on methodology. Gas chromatography equipment suitable for this work has been purchased and will be installed in Germany and France within 1 to 3 months.

4. Monsanto methodology at Ruabon and more recently at Newport is based on work in St. Louis. Ruabon has yet to look at water from estuaries and the sea and wildlife for PCB's.

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origin in the UK and Europe. PCB residues are most typical of Monsanto Aroclor 1254. (March publication in Statens Institut for Folkhalsan, "Levels of Organochlorine Pesticides and Polychlorinated Biphenyls in Margarine, Vegetable Oils and Some Foods of Animal Origin on the Swedish Market -1967-1969", Gunnel Westoo, Koidu Noren and Margit Anderson.

10. PCB's continue to be found in the environment - both in fresh and marine waters and sludge from sewage treatment plants.

11. Chlorinated terphenyls have been identified in herring by Unilever in the UK and presumably by the Folkhalsan Institute in Sweden.

12. PCB's found in dead seals in the UK and birds from the Irish Sea incident are not sufficiently high compared to that in healthy specimens to cause death.

13. PCB's found in nuts and many other foods in the UK have been traced to Littlejohn packaging drums manufactured from NCR broke paper containing Aroclor 1242 sold by Wiggins Teape.

14. The lack of suitable known isomers continues to slow down Monsanto and outside laboratories carrying out analytical, biodegradation and toxicological studies.

15. PCB's were found in fish in the waters of Scotland back to 1963 as shown by examination of old GC curves. No curves available for earlier years.

16. Less than 1% of fish from east and west coast of Scotland contain more than 0.1 ppm PCB with a 0.05 ppm detection limit.

17. PCB's in Scotland appear to be discharged in sewage trade wastes - hundreds of ppm found in sewage sludge - not in effluent or liquors. No problem with fresh water - appears to be marine environment only.

18. The possibility of PCB's being a contaminant in pesticides appears to be ruled out. Reason - in Scotland the PCB's are not always fellow travelers with pesticide residues. Comment was made that only two chlorinated compounds occur in nature.

19. PCB residue results for 5-7" Rainbow Trout exposed to 0.1 ppm Aroclor 1254 were inconclusive. Dead fish after 121 hours contained 15-56 ppm compared to 12-70 ppm for fish which lived.

20. Results of fish studies indicate no biological isomeric change in Aroclor 1254 per GC curves.

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21. Beef, mutton and butter from New Zealand shows no PCB compared to that from the UK.

22. Work is underway at Utrecht on the GC separation and identification of toxic components in PCB's. No GC peaks have yet been found for toxic components (furans) in Aroclor products. Study will be extended to looking for furans in seals and wildlife.

23. General comments suggest that Bayer may be aggressive on substitute products - we were asked if we had considered fluorinated biphenyls.

24. Observations were made that the isomeric composition of Aroclor 1254 changes upon standing in air - presumably due to volatility.

25. A two year study at Monks Wood in England shows that fresh water fish feeding birds contain more PCB than mammal feeding birds. Insect feeders contain the lowest level. (July publication in Environmental Control (?), "Polychlorinated Biphenyls in Wild Birds in Britain and Their Avian Toxicity" by Ian Prestt, D. J. Jefferies and N. W. Moore).

26. Above workers conclude off the record that thin egg shell problem in Britain is due to pesticides and not PCB's.

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May 25, 1970

AROCLOR ENVIRONMENTAL PROGRAM

DETAILED REPORT ON EUROPEAN TRIP COVERING ANALYTICAL PROGRAMS

This report summarizes findings and lists actions planned for world wide Aroclor analytical projects. It covers visits made by Messrs. Papageorge, Wheeler and the writer from May 1 through May 20. It is intended that this report will supplement toxicity, manufacturing and business oriented reports provided by Wheeler and/or Papageorge.

MAY 4 - MONSANTO COMPANY, NEWPORT, WALES

Findings

1. Newport completed the installation of a Hewlett-Packard 402 gas chromatograph with electron capture detector in late April. The analysis of water and mud from the River Severn for PCB's is underway. Early GC data provided by Ruabon show 320 to 2068 ppb PCB in mud from the River Severn around the Newport area.

2. Recovered HCl from Newport operations contains no detectable (< 5 ppb) PCB. Food grade fumaric acid has not been made from HCl for 18 months.

3. Aroclor still bottoms (9600 pounds per year) and filter cake (3600 pounds per year) have been dumped at the Pontypridd commercial land fill disposal site. Analysis of site pools and streams showed less than 4 ppb PCB.

4. At the beginning of 1970, 30 pounds of PCB in one million gallons of effluent were produced by the plant at Newport. The current target is 0.1 pounds per day. No fish from the water around the Newport plant site have been analyzed for PCB. The Ministry of Agriculture has requested that this be carried out.

5. No work has been done on the analysis of air samples from the plant site. Analytical work was carried out to support incinerator studies carried out by Perle Brothers. No PCB's were detected in scrubber tower samples.

6. Currently, there are two analysts handling 14 samples per day for PCB analytical work at Newport.

7. A Hewlett-Packard automatic sampler for gas chromatographic work was observed in operation for 4-nitrodiphenylamine analysis. This unit, which has been in operation 3 months, is the first one in the United Kingdom.

Actions

1. Notify Pat Reagen about recommendation on how to estimate PCB levels, to choose correct sample size and avoid repetitive time consuming GC runs.

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2. Exchange information with Pat Reagen - Doug Casey on use of the Hewlett-Packard automatic GC sampler.

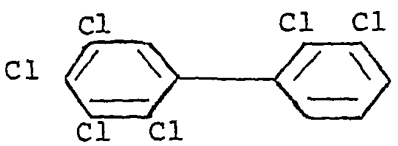
MAY 5 - MONSANTO COMPANY, RUABON, WALES

Findings

1. G. Telling of Unilever Colworth in the United Kingdom has observed chlorinated terphenyls and reported same along with PCB's. Telling is scheduled to visit the Applied Sciences Section in St. Louis on Tuesday, June 2nd. Unilever is the biggest processor of smoked herring in the United Kingdom. Dr. Telling has found PCB's in herring.

2. Comments were made that the Irish Sea incident involving dead birds and the dead seal incident off the coast of the United Kingdom will be covered by reports showing no apparent correlation with PCB residue levels. Starvation is the apparent cause of death. PCB's found resembled the Aroclor 1254 most closely.

3. Cashew nuts in Littlejohn drums were found to contain PCB typical of Aroclor 1242. Analysis of the paperboard in the drums confirmed that it contains PCB. Further work showed that the PCB comes from mill broke which is excess paper material from NCR paper runs. All analytical work done at Ruabon has involved Aroclor 1242 using packed GC columns and methodology developed in St. Louis. No new methods have been developed at Ruabon. Current work is directed toward alternate columns which will be prepared by Ruabon as less costly columns for GC work. Ruabon has yet to look at water from estuaries and rivers in the United Kingdom and no work has been done on the determination on PCB residues in wildlife. Biodegradation work underway at Ruabon was reviewed. Results indicate that degradation occurs at the 2 and 3 chlorine positions on the biphenyl rings. By theory, it is believed that the following chlorinated biphenyl is the highest chlorinated species that will degrade.



Other structures will be isomers produced by taking chlorines from the above structure. The monitoring of degradation work is difficult because the identity of GC peaks has not been made for absolute interpretation of the data. River die-away and two liter semi-continuous sludge laboratory units are in operation.

4. Ruabon has no other biodegradation data on organic compounds relative to the Aroclor environmental project. It was agreed that standard biodegradable procedures for industry use still need to be resolved.

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5. A comparison of available PCB isomers both in St. Louis and Ruabon was made. Ruabon has the 2,2', 4,4', 6,6' hexachlorobiphenyl isomer available. A project which provides a grant of about $2500 for the University of Bangor was approved for the study of organisms which will grow on PCB's.

Actions

1. Prepare agenda for G. Telling's visit on June 2nd.

2. Determine applicability of PCB methodology for chlorinated terphenyls with reference to oral reports by Telling of Unilever to Ruabon.

3. Determine if St. Reagis Paper Company has NCR broke which is made into cardboard containers for the food industry. Obtain and analyze such containers for PCB.

4. Carry out biodegradation program on HB 40 and mono isopropyl biphenyl. Maintain close liaison with Ruabon on HB 40 biodegradation studies which will also be carried out at Ruabon.

5. Firm up isomer availability list between Ruabon and St. Louis and exchange needed isomers.

MAY 6 - DEPARTMENT OF AGRICULTURE AND FISHERIES, SCOTLAND
FRESH WATER FISHERIES, PITLOCHRY, SCOTLAND

Findings

1. The Pitlochry Laboratory is set up with GC electron capture instruments and has no mass spectrometer. The quality of the work done is considered high.

2. PCB's found in fish, birds and seals appear most typical of Aroclor 1254.

3. The laboratory is making a big effort to trace the source of PCB's especially on the analysis of sewage treatment plants effluents and sludge for PCB's. It was observed that the largest Aroclor 1254 GC peak disappears regularly in fish and seals. Comments were made that the Laboratory of the Government Chemist in London could not confirm these observations. The chromatograms are very poor.

4. Comments were made that the seal problem was out of proportion on the seriousness because the PCB levels were not higher in normal seals.

5. A review of chromatograms at Pitlochry back to 1963 shows evidence of PCB's back to this date.

6. The laboratory routinely analyzes herring, mackerel, whiting, cod and similar fish from east and west coast locations for PCB's and pesticides. Less than about 1% contain more than 0.1 ppm PCB's with a detection limit of 0.05 ppm.

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7. Results from analytical programs show lower pesticide levels in estuary water from agricultural areas than from industrial areas. This is the reverse of expectations.

8. The laboratory is not really concerned about PCB's, per se, but is very concerned about how PCB's get through the water sources. Direct discharge into sewage treatment wastes seems to be the route. It has been observed that PCB's are not found in sewage effluent or liquors - only the sludge. Hundreds of ppm apparent Aroclor 1254 have been found in the sludge. The pesticide levels run lower. The sludge is discharged at sea. There is no problem with fresh water sources - it appears to be concentrated with the marine environment only.

9. PCB's are not always fellow travelers with pesticides. Conclusion - PCB is not a likely contaminate at very low levels in pesticide products.

10. The comment was made that only two chlorinated compounds occur in nature.

11. The results of a fish toxicity study using Aroclor 1254 and rainbow trout were discussed. A solution of water containing 0.1 ppm Aroclor 1254 was prepared using 10 milliliters of 40 ppm Aroclor 1254 in acetone. The level of Aroclor was checked every two hours by GC. More than 1/4 of the amount of the Aroclor disappeared in 24 hours. A new solution of freshly prepared Aroclor 1254 and water was recharged every 24 hours. Twenty fish, size 5" to 7" in length, were put in the above water solution. Results showed that 7 of the fish died after 121 hours with levels ranging from 15 to 18 ppm PCB in the muscle and 45 to 56 ppm in the viscera in the dead fish. Remaining fish which lived 192 hours contained 12 to 14 ppm PCB's in the muscle and 64 to 70 ppm in the viscera. This report was qualified with the comment that Whitehall Laboratories took much longer to kill the fish under similar conditions. They made no analyses of the fish for PCB residues.

12. Examination of the chromatograms from the fish toxicity study show no evidence of degradation of Aroclor 1254. This suggests no isomer change in this one biological system.

13. The Pitlochry Laboratory uses hexane soxhlet extraction of fish made up with sodium sulfate to obtain 100% recovery.

Actions

1. Investigate the need for soxhlet extraction for complete recovery from PCB from tissues compared to our present cold extraction method.

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MAY 8 - WIGGINS TEAPE/A. D. LITTLE, LONDON, ENGLAND

Findings

1. Wiggins Teape summarized analytical data obtained for Littlejohn cardboard drums which showed the presence of Aroclor materials in the cardboard drums and products therein, Aroclor was found in products such as bicarbonate of soda, cream of tartar, sage, white pepper and salted peanuts. A summary of these findings is attached.

2. The availability of pure isomers for toxicity work and metabolic studies was discussed. We emphasized the difficulty in preparing sufficient amounts of isomeric materials of this type.

Actions

1. Confirm the presence of PCB in food products in the United States in containers known to be packaged in containers manufactured with paper or cardboard containing PCB products.

MAY 8 - THE LABORATORY OF GOVERNMENT CHEMISTS, LONDON, ENGLAND

Findings

1. The Government Laboratory still finds PCB's in wildlife specimens from the United Kingdom. PCB's are occasionally found in cow's milk at very low levels. PCB's are sometimes found in beef and mutton fat. There are a few indications of PCB at the 0.1 ppm level typical of Aroclor 1254 or 1260 in human fat.

2. Terrestrial birds of prey and herrings show the highest PCB levels. Herring liver has been found to contain as high as 100 ppm.

3. The Laboratory of the Government Chemist is supportive to other laboratories of the government. For this reason, the total project was not always understood and results found could not be used to make conclusions.

4. Beef kidney fat, mutton kidney fat, and butter from New Zealand show no evidence of PCB's. Findings reported are for samples from the United Kingdom.

MAY 11 - INSTITUTE OF VETERINARY PHARMACOLOGY AND TOXICOLOGY, UTRECHT, NETHERLANDS

Findings

1. Chlophan A-60 was fractionated to obtain quantities of toxic materials. Components separated by GC were identified by mass as furan type materials. Aroclor products showed no peaks which could be correlated with toxic components as determined by testing with chicken eggs. The question of generation of dioxin materials from the burning or pyrolysis of wood containing pentachlorophenol was raised. This institute is interested in carrying out such

1. (Continued)

experiments if this project has not already been scheduled. It was also agreed that we would provide dioxin reference materials for their use when available.

2. This institute is now looking for furans of the type that would be in polychlorinated biphenyls in seals and wildlife.

3. The need for isomeric materials for reference purposes for the study and analyses of Aroclor products was raised. It was revealed that synthesis work on some of the major isomers is underway at this institute. The parties responsible for this work will contact the writer in the interest of exchanging reference materials to provide a more complete set of standards.

Actions

1. Correspond with this institute and arrange for exchange of reference isomers as standards for methodology purposes.

2. Follow up on exchange of wildlife materials or extracts thereof to provide information obtained in our own laboratory as to the level of PCB's in wildlife.

MAY 12 - THE STATENS INSTITUT FOR FOLKHALSAM, STOCKHOLM

Findings

1. Dr. Westoo reported on levels of organo chlorine pesticides and polychlorinated biphenyls determined in about 1400 samples of margarine, vegetable oils and foods of animal origin from 1967 thru 1969. About 90% of the food samples investigated contained at most 0.1 milligram per kilogram of PCB. The attached English summary and tables are from a March, 1970 publication covering this work.

2. Dr. Westoo made a plea for standard isomeric components to obtain better analytical data for the PCB products.

3. It was apparent that Dr. Jensen was behind the scenes in this work in that the reference PCB materials for the analytical work was provided as synthetic mixtures of PCB isomers by Dr. Jensen. No mass work was done by Dr. Westoo to confirm the chromatograms.

4. Chromatograms provided by Dr. Westoo were reported as those for Aroclor 5460. Dr. Westoo apparently was not aware that 5460 is a chlorinated terphenyl product. A copy of the chromatogram and the solid Aroclor product used was obtained and brought back for confirmation. Little work has been done in our laboratories to date on the determination of the chlorinated terphenyls in natural products.

5. The conclusion of the report mentioned above is that there is not too much PCB's in food stuffs, however, there still has to be an effort to get less in the environment. Fish and meat for human

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5. (Continued)

consumption are the greatest problem areas for PCB's. Fish from the Baltic Sea has the highest level. This laboratory has written to several government authorities about the PCB problem. It has the power to recommend only and not to enforce.

6. The food materials reported were obtained locally in Stockholm. A task group is still in operation on the PCB problem.

Actions

1. Chromatograph the Aroclor 5460 used at the institute and determine methodology needed to measure the chlorinated terphenyl components. Evaluate the data reported from results obtained in our laboratory.

MAY 12 - INSTITUTE OF ANALYTICAL CHEMISTRY, UNIVERSITY OF STOCKHOLM

1. Professor Widmark commented that about 1500 routine analyses have been turned out by the institute during the past year to provide financial support. Without this activity the institute would have undergone financial ruin, according to Widmark.

Widmark is currently removed from the PCB picture by his inactivity during the past year on problems of this type. His current interest is more on fundamental research on 10 year programs directed toward data acquisition and computerized mass spectrometry. A major portion of this effort is being supported by the tobacco institutions with work directed toward flavor and aroma components.

3. Widmark is especially interested in more complete separations of components such as isomers in our PCB products and smoke by glass capillary columns. It was suggested that we would arrange for him to talk with our experts in St. Louis when he visits us on June 3.

4. Widmark could not report results of his analyses because of confidentiality requested by the submitters. He continues to believe that more positive identification is needed on the PCB problem. The treatment of samples for removal of interfering components needs additional attention.

5. Widmark commented that the buyer is apparently on substitute products. No details about type or direction of their program was mentioned.

6. It was agreed that Professor Widmark will give a seminar in St. Louis on June 3 entitled, "Identification of Unknowns Using Gas Chromatography - Computerized Mass Spectrometry".

Actions

1. Arrange details for Professor Widmark's visit on June 3 and set up agenda.

MAY 13 - LILJEHOLMENS, STOCKHOLM

Findings

1. The state of the analytical program was discussed in general with this customer. A tour of the manufacturing facility was made with a special reference to the handling and disposal of Aroclor used in their electrical products.

MAY 14 - BRUSSELS MEETING WITH BAYER, PRODELEC AND CAFFARO

Findings

1. Manufacturers in Germany, France and Italy are equipment-wise and method-wise at the point where we were one year ago. Bayer and Prodelec plan to start up GC equipment which is on order within one month. Bayer reported that residue work and toxicity work with fish and residues related thereto has been delayed some months. Long term feeding of mammals has been started.

Actions

1. Our methodology package will be sent to these laboratories via Ron Lidgett within seven days after the meeting.

MAY 15 - BAYER, LEVERSKUSEN, GERMANY

Findings

1. After visiting the Bayer incineration plant, a visit was held with Dr. Rickert who is head of the organic analytical laboratory. This operation is in an 8 story building and consists of 450 employees carrying out analytical work on Bayer's organic products.

MAY 18 - MINISTRY OF AGRICULTURE, FISHERIES AND FOOD, BURNHAM ON CROUCH, ENGLAND

Findings

1. This laboratory plays a coordinating role to determine primarily how PCB's get into the environment. They monitor fish, food and sludge products. They overlap with the activities of Dr. Holden at the Department of Agriculture and Fisheries in Scotland. This laboratory has examined fish from the west and east coasts of the United Kingdom. Also, it has looked at birds in the United Kingdom and the mortality of same is one of their problems.

2. The significance of PCB in marine organisms is under study. Current findings suggest that the PCB problem is a marine problem and not a fresh water problem. Chromatograms for fish, shrimp, etc., resemble 54% chlorinated biphenyls. How widespread the problem is for PCB's in non-industrial areas is yet to be determined. It appears to be associated with industrial areas. A forward program of this laboratory will be to look at fish from non-polychlorinated biphenyl areas. They will be monitoring industrial estuaries for PCB and pesticides. Muscles from the Bristol channel will be examined.

Actions

1. Fish samples from the Bristol area will be exchanged with Monsanto via Ron Lidgett for determination of PCB's.

2. Methodology for PCB's will be forwarded to this laboratory via Ron Lidgett.

MAY 19 - THE NATURE CONVERSARY MONKSWOOD EXPERIMENTAL STATION, ABBOT'S RIPTON, HUNTINGTON

Findings

1. The Monkswood laboratory concentrates it's efforts primarily on the study of the effect of pesticides upon wildlife. This includes birds of prey and sea birds. They are currently interested in PCB's in Guillimots. They have analyzed the livers of hawks, owls and herons for pesticides at the rate of 250 samples per year since 1963. Results for 559 wildlife species of birds which were analyzed from April 1966 to 1968 for PCB is being published in the July issue of Environmental Control(?). This article is entitled "Polychlorinated Biphenyls in Britian and Their Avian Toxicity", by Ian Prestt, D. J. Jeffries and N. W. Moore. The summary page from this publication is attached. The objective of this study was to categorize PCB levels geographically and by feeding habits of birds. The highest levels of PCB's ranging from 6 to 900 ppm in the liver were found in fresh water fish feeding birds. The high level in fresh water fish feeding birds is a surprise. The level in hawks, falcons and mammal feeding birds was the next highest. The insect feeding birds contain the lowest level of PCB ranging from 0 to 1 ppm. The mammal feeding birds contain from 0 to 50 ppm PCB. Work will continue on analysis of birds from the United Kingdom for some years to come. The levels of PCB in heron eggs are lower than DDT and Deoldrin. The PCB found in birds at this laboratory resemble our Aroclor 1254 product.

2. Bengalese Finches toxicity studies were carried out with Aroclor 1254. Seven birds that died after 56 days contained 70 to 697 ppm PCB in the livers. The 20 birds used for the study contained 3 to 634 ppm in the livers. Results needed for correlation with death are inconclusive.

3. No work has been done in this laboratory on fish analysis.

4. Chromatographic data from the bird studies shows no evidence of isomeric change in residues from the Aroclor 1254.

5. Isomeric changes were observed from Aroclor 1254 after standing in air presumably caused by volatility losses.

6. Experimental work with insects (butterflies) showed no longevity or reproducible effects with near lethal doses of Aroclor 1242. No PCB residues (less than 0.02 ppm) were found. This correlates with the low residue level in birds which are insect feeders.

This laboratory has shifted future emphasis from lethal to sub-lethal PCB studies.

8. The Laboratory of the Government Chemist carried out the gas chromatographic analyses for the publication mentioned above. Earlier comments lead to questions about the accuracy and competency of this laboratory. The findings reported in the above publication will be no better than the quality of data provided.

9. The people at Monkswood are confident that DDT and DDD are responsible for thin egg shell effects in Britian and not the PCB's.

Actions

1. Increased emphasis should be put on our Bio-Test tissue analysis program to correlate residue levels with toxicity data. These workers feel this is a very important piece of information for the total program.

MAY 20 - MINISTRY OF AGRICULTURE, FISHERIES AND FOOD - PEST INFESTATION CONTROL LABORATORY, TOLWORTH, ENGLAND

Findings

This laboratory became involved with PCB's through the Irish Sea incident. The investigation was primarily analytical.

2. A mass spectrometer has been purchased to be delivered in six months for more sophisticated studies of pesticides and PCB materials.

3. This laboratory is getting geared to do more sophisticated metabolic studies involving chlorinated materials including PCB's with known isomers.

4. A survey has been made and work started on the preparation of known PCB isomers for correlation of alteration of biological conditions with structure. Three to five gram quantities will be prepared. Specific isomers have not been selected for this synthesis work.

5. This laboratory has not been able to obtain the same answers for PCB's and birds as reported by the Laboratory of the Government Chemist. They have not seen chromatograms from the Government Chemist and commented that recent personnel changes have been made with less competent people involved.

6. The finding of PCB in cashew nuts was reported on with subsequent identification in packaging materials (Littlejohn drums). This observation of PCB in food packaging materials has been prepared as a note to the editor for publication within the next several weeks in one of the technical journals. This note is attached.

7. This laboratory uses cold acetone to extract PCB from tissue which reduces fat interferences. Comments were made that this could shorten methodology time considerably.

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8. Comment was made that chlorinated biphenyl containing a methyl group should be considerably more biodegradable. Copies of methodology have since been forwarded to the writer in St. Louis.

Actions

1. Evaluate cold acetone extraction as an improved shortened analytical method for analysis of 1000 cubic meters of tissue in St. Louis. Significant reduction in analysis time can mean thousands of dollars saved on this part of the program.

R. E. Keller

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