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REPORT OF THE AD HOC SUB-GROUP ON TRACE ORGANIC COMPOUNDS
UNDER THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, February 24-25, 1985

The Chairman of the ad hoc Sub-Group on Trace Organic Compounds, Dr L Reutergårdh, opened the meeting at 9.30 hrs on February 1985 and welcomed the participants.

The agenda of the Sub-group was identical to its terms of reference (C.Res.1984/2:21), which were sent in advance to all of the members:

- (i) To consider papers prepared before the meeting describing advances in analytical methodology for PCBs and other chlorinated hydrocarbons;
- (ii) to review and evaluate the results of the intercalibration for PCB congeners being coordinated by Dr L Reutergårdh;
- (iii) to review and evaluate results of methodological studies for chlorinated hydrocarbon analysis, in particular the study being conducted within the European Community;
- (iv) to recommend specific actions to improve the analysis of PCBs in environmental samples.

J Utte introduced his paper "Identification of error in the interlaboratory comparative study of the determination of chlorobiphenyls in fish oil" (see references). He focused attention on the following issues.

- the care necessary in the preparation of standard solutions
- the identification and quantification problems which may be caused by co-eluting CBs and other interferences
- the necessity of the use of multi-column analysis
- that most of the total error is a systematic error, which results from procedures used prior to the gas chromatographic stage of the determination.

In the discussion the necessity for standards, which have been certified qualitatively as well as quantitatively, was recognized. Doubts came up about the accuracy of retention indices, although the paper by M Mullin et al. (see references) mentioned that the separation of 187 PCB congeners is possible on a 50 m SE-54 column. It was not expected that all analysts could be able to reproduce this result in their routine procedures.

Almost all of the representatives used liquid coating of two polarities: dimethylsilicones (SE-30) or methylphenylsilicones (SE-54). Those columns seem reproducible in the elution order of all chlorobiphenyls if one uses a fixed temperature program. Retention indices may differ, especially with changing temperature programs. It depends on the precision required for a study, as to whether this is acceptable or not. Retention indices appeared to change in samples that have not been properly cleaned; especially lipids seem to be of influence. D Wells informed the Sub-Group that a

series of homologue dichlorobenzyl-alcohol-ethers have been synthesized in his laboratory for the development of a retention indices system. Some of these dichlorobenzyl-alcohol-ethers can also be used as internal standards for the correction of the GC injection.

M Kerkhoff presented her paper(see references) on the use of certain PCB congeners in environmental studies. A list of 7 chlorobiphenyls from tri- to hepta-chloro was suggested on the basis of four criteria:

- presence in industrial mixtures of different degrees of chlorination
- occurrence in environmental samples
- toxicity of individual chlorobiphenyls
- analytical performance

For ordinary pollution studies the 7 chlorobiphenyls (IUPAC numbers 28, 52, 101, 118, 138, 153, 180) used in the Netherlands for tolerance purposes are suggested, realising that for special studies another choice may be preferable.

Questions arose about the toxicity studies reported in the literature. The ideas about the toxicity of PCB are mainly based on data on enzyme induction and it was recognised that there is a lack of information on the real toxicology of CBs. The importance of oxygenated metabolites of chlorobiphenyls in respect to their suspected chronic toxicity was reported by J Calder from a study by R W Gossett (see references).

D Wells supported the list of chlorobiphenyls as a good basis for monitoring exercises. The Community Bureau of References of the European Community (BCR) has demonstrated the progress that can be made by focussing the analysis on a few selected chlorobiphenyls. In a paper by L Tuinstra (see references) about the last BCR results the improvement of analytical performance is mentioned by using prescribed test procedures for optimization of gas chromatographic settings for splitless and on-column injection. In a study with cleaned eel-fat extracts a CV(R) ranging from 11 to 24% was obtained.

Several important parameters for the analyses have been discussed:

- initial column temperature
- injector temperature and valve closing time in relation to discrimination problems and peak shape
- choice of the polarity of the stationary phase
- the use of an internal standard - 2,4 dichlorobenzylalcohol ether C-14 appeared to be the best one
- the presence of negative peaks
- advantages and disadvantages of mobile phase H₂/He
- linearity and stability of the ECD detector, common cleaning procedures, the avoidance of oxygen
- the use of other detection systems like mass spectrometry with electron impact and negative chemical ionization (fullscan as well as selected ion monitoring).

L Reutergårdh (see references) presented the results of the interim study on chlorobiphenyls in herring oil. The poor responses of several collaborating laboratories in meeting the deadline delayed the evaluation of this study from 1984 to 1985. The coefficients of variation for chlorobiphenyl analysis in fish oil appeared to decrease compared to earlier studies, but this decrease is still not sufficient. For future work it was suggested that recoveries should be reported and only values corrected for recovery should be used. It was recommended that a large batch of a technical PCB mixture and several chlorobiphenyls should be made available as reference and standard materials.

Several technical questions arose again, which all indicated the need for good laboratory practice to guarantee the quality of analytical data. Information about these subjects can be obtained from the BCR studies. A duplication of the BCR work by ICES was considered of less relevance than the optimization of ICES laboratories according to guidelines which have been published in the open literature:

- optimization of the equipment
- optimization of detection and injection techniques
- a study of the reproducible production of standard solutions.

After the first day's meeting in plenary, certain problem areas were identified:

- 1) Reference materials and certified standards are needed for self check and better performance, both in cooperative monitoring studies and in intercalibrations, not only for CBs but other organic compounds of environmental concern.

- 2) The question was raised as to whether some laboratories had continuously reported values closer to the true value during past intercomparison exercises, and if these laboratories could be identified. If so, these laboratories should participate in an intercomparative study to determine to what extent the coefficients of variation could be decreased.
- 3) A list of reminders for "good laboratory practice" should be made and circulated to the laboratories to enhance their work before the analysis of references or monitoring samples.
- 4) A recommendation, concerning which chlorobiphenyls should be suggested for PCB analysis was needed. Coelutions of CBs on different liquid phases should be considered as well as whether further studies of technical products are necessary or whether the present knowledge is sufficient for the time being.

These subjects were discussed in three Sub-Groups.

Sub-Group 1

The Sub-group consisted of J Calder, J Farrington, J Uthe, and E Huschenbeth.

Draft Recommendations for Standards and Reference Materials for Trace Organic Analysis in Support of the ICES Coordinated Monitoring Programme.

1. The Marine Chemistry Working Group should encourage participating laboratories to obtain the necessary standards from one or more of the following sources for purposes of proper instrument calibration:

- The National Research Council of Canada has available for purchase (\$100 U.S.) 51 chlorobiphenyls in 4 solutions of iso-octane, each containing a mixture of CBs easily resolved by capillary gas chromatography on SE-54.

Contact: Roger Guevremont (phone:902-426-8280)
NRC Canada
Atlantic Research Laboratory
1411 Oxford Street
Halifax, N.S. B3H 3Z1
Canada

- the Community Bureau of References (BCR) will have available 10 chlorobiphenyls at the end of 1985 (IUPAC No's 8, 20, 28, 35, 52, 101, 118, 138, 153, 180). A set of 30 mg each will be sold for 3000-5000 Francs (Belgium);

Contact: Community Bureau of References (Telex: 21877)
COMEU B) (phone: 235-1111)
Rue de la Loi 200
B-1049 Brussels
Belgium

- The U.S. National Bureau of Standards soon will have standard solutions of CBs available for purchase.

- other organochlorines (e.g. pesticides) and PAHs can be purchased from various private suppliers.

2. The MCWG should identify a single coordinating laboratory to prepare and distribute the following reference materials:

- Reference materials (RMs) for common organochlorine pesticides, chlorobiphenyls, polynuclear aromatic hydrocarbons at various levels and in various matrices
 - * a fish oil (cod liver or herring) and a shellfish tissue, selected on the basis of information already available to ICES, should be prepared (2000 packages of each, 50g dry weight per package) Approximately 200 packages will be needed for time and inhomogeneity studies.
 - * a mechanism is needed to assure a long-term supply of the RMs to ICES laboratories.

- For immediate use in 1985 the following RMs should be obtained
 - * a single large batch of Aroclor 1254 or equivalent can be provided by Jack Uthe
 - * a frozen mussel homogenate, available from the U.S. NOAA (shipping problems may interfere).

- 3. The coordinating laboratory should select, according to National Bureau of Standards or other rigorous criteria, several "checkers" to obtain the best estimate of the concentrations of the analytes in the RMs. RMs should then be used by all ICES laboratories to demonstrate ability to analyze satisfactorily for the analytes. Prior to this demonstration, ICES should attempt no further intercomparisons for organics. (It is noted that activities underway within the BCR will provide information on interlaboratory comparability for several

of the ICES laboratories.) About 1 year after the RMs become available, and if a number of laboratories are unable to achieve satisfactory results, ICES should sponsor a training workshop.

Sub-group 2

The Sub-group consisted of D Wells, M Pertillä, R Law and M O'Sullivan.

Analysis of Organochlorines in Biological Tissue by Capillary GC

1. General Materials should be checked for purity of each batch, e.g., solvent, sodium sulphate.
2. Sample Preparation and Extraction Batches of 10 + Blank + External Standards at 2 concentration levels (with matrix if/when available)
3. Preparation of Standard
 1. Calibrate balance
(not certify!)
 2. Have weights checked
 3. Define life time of standard solutions
 4. Check each weighing
 5. Keep checked records of solution weight, check dilution and solvents
 6. Calibration by weight
4. Clean-Up and Fractionation each batch prepared and tested for quality/purity
5. Analysis by GC
Quality of instrument/gases/Laboratory conditions

Optimisation - injector conditions
programme rate (LT)
resolution check/detector for response check
Linearity-plot height/width vs. width (10 points)

6. Methods of Identification

Relative retention time (RRT) or Relative retention index (RRI) on at least two phases
RRI can be stored in data base
Confirmation by GC-MS

7. Methods of Quantification

Use internal standard at this stage
Quantify, ideally on at least 2 standards bracketing the concentration of the sample.
Inject standards every 5/6 samples in Automode Beginning/End of day for manual injection.
Check computer/integrator performance

8. Documentation and Verification

Record all measurements in appropriate book/file
Check each blank, external standards for each component
Flow chart and progress at each stage

Reference: Organic Trace Analyses - K Bayermann and Ellis Harwood (1984). This subject area has been presented in far more effective detail elsewhere in the open literature.

Sub-Group 3

Sub-Group 3 consisted of L Reutergårdh, K Palmork, A Abarnou and M Kerkhoff

The Sub-Group discussed whether there was a need for further studies on the identification and quantification of

technical mixtures. Although this was considered of importance, it was recognised to be of no relevance for the selection of specific chlorobiphenyls because at the moment there is enough agreement about the major chlorobiphenyls.

Referring to the paper of M Kerkhoff, page 6, the Sub-group agreed to the following paragraph, "The decision, which congeners have to be quantified, depends on the purposes of the planned study. An extraordinary contamination with PCBs of special chlorination pattern, may influence the choice of congeners. Also special studies on bioaccumulation, degradation or metabolism will meet other requirements than common pollution studies."

When restricted to ordinary pollution situations the Sub-group recommended the list of 7 chlorobiphenyls mentioned in M Kerkhoff's paper as a first selection:

IUPAC Nos. 28, 52, 101, 118, 153, 138, 180

The Sub-group also made a second list with other important chlorobiphenyls which can be used together with the first selected chlorobiphenyls:

18, 31, 44, 66/95, 110, 149, 187, 170

Furthermore the Sub-group recommended that more studies are required about chlorobiphenyls of environmental concern, for instance, toxic CBs or unidentified major CBs. Analysts with mass spectrometers are recommended to perform analyses on coeluting and interfering compounds occurring in samples from the ICES areas and to supply their results to ICES.

The recommendations which can be given to MCWG and WGMPNA in respect to the inclusion of organochlorines in the 1985 Baseline Study of Contaminants in Fish and Shellfish were

discussed in plenary. Although some progress has been made in organochlorine analysis, the Group felt unable to change the advice given at last year's MCWG meeting, quoted as follows:

"Because of the limited number of laboratories capable of doing chlorinated hydrocarbon analysis with sufficient reliability, the Sub-Group suggested that for the 1985 Baseline Study, samples from a wide area be sent to these laboratories for analysis to determine levels and large-scale distribution of chlorinated hydrocarbons, especially PCBs. Other laboratories that wish to conduct analyses of PCBs and other chlorinated hydrocarbons should not be discouraged from doing so, but should be encouraged to analyse samples from as wide a geographical area as possible to permit an overlap of areas sampled by other laboratories."

After the discussion on the organochlorines was finished, two other papers were presented on the results of intercomparison exercises on the analysis of polycyclic aromatic hydrocarbons and petroleum hydrocarbons in biological tissue:

J Uthe: Report on the intercomparative study O3/HC/BT on the determination of polycyclic aromatic hydrocarbons in biological tissue

J Farrington: ICES/IOC Intercomparison exercises on the determination of petroleum hydrocarbons in biological tissues (mussel homogenate) - ICES (2/HC/BT)

REFERENCES

- Farrington J W, A Knap, A C Davis, J B Livramento, CH Clifford, N M Frew - ICES/IOC Intercomparison Exercises on the Determination of Petroleum Hydrocarbons in Biological Tissues (mussel homogenate) ICES (2/HC/BT)
Draft final report MCWG 1985 Copenhagen
- Gossett R W, D A Brown, S R McHugh, A M Westcott
Measuring the oxygenated metabolites of chlorinated hydrocarbons
Biennial Report 1983-1984, Southern California Coastal Water Research Project, ed. W Bascom
- Kerkhoff M A. Suggestion for the use of certain PCB congeners in environmental studies
ICES/MCWG 1985/8.2 + ad hoc Sub-group meeting on trace organic compounds
- Mullin M D, C M Pochini, S McCrindle, M Romkes, S H Safe and L M Safe
High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of all 209 PCB congeners
Environ. Sci. Technol. (1984) 18, 468-476
- Reutergårdh L, K Litzen
Report on an intercomparison study of the determination of polychlorinated biphenyls (PCB) isomerids in Baltic herring oil
ICES/MCWG 1985/8.2 + ad hoc Sub-group meeting on Trace Organic Compounds.
- Tuinstra L G M Th, A H Roos and B Griepink
Interlaboratory studies of the determination of some PCB congeners with capillary gaschromatography using splitless- and on-column injection techniques
Will be presented at the 6th International Symposium on Column Liquid Chromatography, Riva

del Garda, 14-16 May 1985. This paper is made available as preprint only for purposes of ICES/MCWG

Uthe J F, R K Misra, C J Musial.

Identification of error in the interlaboratory comparative study of the determination of chlorobiphenyls in fish oil

ICES/MCWG 1985/8.2.1/1

Uthe J F, C J Musial, G R Sirota

Report on the Intercomparative Study O3/HC/BT on the determination of polycyclic aromatic hydrocarbons in biological tissue

ICES/MCWG 1985/8.2.3.

ANNEX 1LIST OF PARTICIPANTS

Abarnou A	France
Calder J A	U.S.A.
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Huschenbeth E	Federal Republic of Germany
Kerkhoff M	Netherlands
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O'Sullivan M	Ireland
Palmork K H	Norway
Perttilä M	Finland
Reutergaardh L (Chairman)	Sweden
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