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REPORT ON FURTHER INTERCALIBRATION ANALYSES IN ICES POLLUTION MONITORING AND BASELINE STUDIES

by

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INTRODUCTION

The results obtained from several earlier series of intercalibration exercises conducted by ICES for the analyses of heavy metals and organochlorines were described in an earlier report (Topping and Holden, 1978). In the light of the experience gained from these exercises, the ICES Working Group on Pollution Monitoring and Baseline Studies in the North Atlantic decided that further intercalibration sampled for lead and cadmium should be distributed during 1977/78, and subsequently an exercise covering a wider range of elements was conducted in 1978/79. At the same time, a new intercalibration sample for organochlorine analysis was prepared and distributed containing lower concentrations of residues than the previous samples in accordance with the decision of the Working Group.

As the samples used and analytical techniques involved in the determination of the two types of residues are quite unrelated, the first section of the report deals with the trace metal analyses and the following section with those for organochlorine residues.

PART I - METALS

INTRODUCTION

During 1972-76 ICES Working Group responsible for pollution baseline and monitoring studies in the North Sea and North Atlantic organised three trace metal intercomparison exercises for biological tissue. The results of these exercises, together with the results of the two intercalibration exercises for organochlorines, are given in ICES Cooperative Research Report No.80 (Topping and Holden, 1978). The trace metal exercises revealed the following:

(1) Throughout these exercises there had been a progressive improvement in analytical performance of laboratories which had participated in more than one exercise.

(2) On the basis of the results of the third exercise it was concluded that the majority of participants in the 1975 ICES fish baseline study produced comparable data for Cu, Zn and Hg.

(3) Considerably more work was needed on the analytical techniques for Cd and Pb before the results from the majority of laboratories were comparable.

(4) Further intercalibration exercises were necessary to monitor analytical performance for Cu, Zn and Hg and to assess the extent of subsequent improvement in respect of the analysis of Pb and Cd.

At the third meeting of the ICES Working Group on Pollution Monitoring and Baseline Studies in the North Atlantic in May 1977 it was agreed that a further intercomparison exercise for lead and cadmium should be organised during the 1977/78 period, to assess the improvements in analytical performance that had been made for these metals following the publication of the report on the third exercise. A preliminary

report of this fourth exercise was presented to the 4th meeting of the above Working Group in May 1978 by the Coordinator (G Topping). At this meeting details of the plans for the 5th ICES trace metal intercomparison exercise for biological tissue, which had been agreed in principle at the 3rd meeting of the Working Group, were also discussed. This 5th exercise was to serve the laboratories in Europe which were taking part in the Oslo/Paris Commission's Joint Monitoring Programme (JMG) and those laboratories which were currently participating in the ICES Coordinated Monitoring Programme.

This report presents and discusses the results of the 4th and 5th ICES trace metal intercomparison exercises for biological tissue.

PREPARATION AND DISTRIBUTION OF REFERENCE MATERIALS

4th Exercise

In June 1977, 20 g of fish flour (the same batch of material as that used in the 3rd ICES exercise) was sent to 18 laboratories in Europe, USA and Canada with instructions to analyse the sample for Pb and Cd only and return the results by 1 November 1977. The participants were also asked to provide details of their analytical techniques and instrumentation and to calculate detection limits for each metal.

5th Exercise

The two reference samples were prepared from a batch of young cod (ca. 250 kg) caught in the inshore waters of Shetland. The fish were filleted, skinned and then cut into small pieces (ca. 3 cm x 3 cm). The major portion of this material (ca. 90%) was freeze-dried and then ground in a hammer mill to produce a fine flour (Sample A). Prior to freeze-drying and grinding the remaining portion, it was subjected to an acid washing procedure to remove some of the mercury in the tissue (Sample B).

It was agreed at the meeting in May 1978 that samples of the reference materials should be despatched to participants in the first week of September 1978, and that a deadline of 1 December 1978 should be set for receipt of analytical data. At the end of August 29 laboratories had notified the author of their willingness to participate in the exercise; these laboratories were sent samples of the reference materials (30 g of 'A' and 5 g of 'B') on 4 September 1978. Between September 1978 and January 1979 a further 20 laboratories were sent samples of reference material, following a circular letter sent by the ICES General Secretary and receipt of a list of JMG laboratories from the Secretary of the Oslo/Paris Commission. Samples of this reference material were also sent to 3 Australian and 4 United Kingdom analytical laboratories which had expressed interest in this intercomparison exercise. In view of the protracted despatch period and the fact that some laboratories, which had received samples in September, failed to meet the agreed deadline of 1 December 1978 the author had little alternative but to extend the deadline, for a further 3 months, to 1 March 1979.

Each participant received a set of instructions (Appendix I) in relation to (a) the range of metals to be examined, (b) the number of replicates required, (c) the calibration procedure and (d) the reporting of data.

RESULTS

4th Exercise

The list of participants and their affiliation are given in Table 1. Analytical results for lead and cadmium (means, standard deviation and coefficient of variation) are given in Table 2.

Lead

Mean concentrations of lead in the fish flour reported by the twelve laboratories ranged from 0.030 to 3.08 µg/g (Table 2). Four laboratories (1, 6, 7 and 12) produced results which were higher than those of the rest and two laboratories (4 and 8) produced lower results. The mean values from the remaining six laboratories (in reality seven sets of analyses since Laboratory 5 submitted two sets of data) ranged from 0.51 to 0.68 µg/g. It is clear that the within-laboratory variability is not the same throughout. In particular the variability for Laboratory 3 was much higher than the others, owing largely to the presence of a single outlying value (1.18). The variability in the data from the remaining five laboratories was more consistent. The differences between the mean values of these five laboratories may therefore be compared using a standard analysis of variance. This test showed that there were significant differences (5% level) between the six sets of data and a multiple range test (Appendix II) was computed to quantify the differences. The results are summarised below:

5a	10	11	5b	9	2
0.51	0.51	0.60	0.63	0.66	0.66

(KEY: Any two or more mean values underlined by the same line are not significantly different.)

It is interesting to note that the means of the two sets of data supplied by Laboratory 5 (resulting from two different methods of analysis) differ significantly, set b) the 'extraction' method (see Appendix II) giving the higher results.

Cadmium

Mean concentrations of cadmium in the fish flour reported by the twelve laboratories ranged from 0.022 to 0.208 µg/g (Table 2). Two laboratories (11 and 12) recorded means which were much higher than the rest. The results from Laboratory 12 were consistent but, in the results from Laboratory 11, there was an outlying value which led to a relatively high coefficient of variation. Within-laboratory variability differed widely between laboratories. This is illustrated by the coefficients of variation given in Table 2. Laboratory 1 quoted results of the analysis to one significant figure only, hence masking any variability in the determinations made. Three laboratories (2, 5b and 8) with coefficients of variation of less than 10% recorded rather different mean levels of cadmium in the fish flour sample, ie 0.030, 0.022 and

0.051 µg/g respectively. The large differences in within-laboratory variability referred to above make it impossible to carry out a reliable analysis of variance to test differences between the mean values.

It was generally agreed at the third meeting of the ICES Working Group that the results for cadmium and lead from the third ICES exercise were relatively poor because the majority of participants were using analytical procedures with high detection limits. The laboratories were asked to review their methodology with a view to improving them. In the light of this request, and by comparison with the methodology used in the third ICES exercise (Topping and Holden, 1978) an examination of the methods used in the current exercise (Appendix III) shows that nearly 50% of the laboratories who participated in both exercises have responded to this suggestion. A comparison of the two sets of data for 1975 and 1977 for cadmium and lead (Table 3) and the reported detection limits (Table 4) shows that those laboratories which made major modifications to their analytical procedures recorded lower mean values for cadmiun and lead and reported improved detection limits. Two laboratories which did not make the suggested changes to their procedure produced values for cadmiun and lead which were similar to those reported by them in the third exercise. The overall mean values for lead and cadmium in this exercise are lower than the overall means obtained during the third exercise (Table 3).

Although the statistical analyses described above show that there are significant differences between the data from individual laboratories, it is clear that the group is progressing towards the production of comparable data for these two metals at the concentrations encountered in this particular reference sample.

5th Exercise

The participants and their laboratories, together with their identification numbers, are listed in Table 5; for reference a second list (Table 6) has been produced identifying those laboratories in Table 5 which had taken part in previous ICES intercomparison exercises.

The results reported by all laboratories are presented in Tables 7-18. Each table shows the number of replicates performed by each laboratory, the minimum, maximum and mean value of each metal and the coefficient of variation. The results are tabulated in order of ascending mean value.

Arsenic

Sixteen laboratories reported data for this element; mean values ranged from 0.5 to 20.7 µg/g (Table 7). Eleven laboratories (17, 35, 41, 19, 2, 31, 20, 39, 21, 23 and 4) reported relatively high mean values of 12.2, 12.9, 13.6, 14.0, 15.5, 15.7, 16.2, 17.0, 18.8, 20.2 and 20.7 µg/g respectively; three laboratories (12, 8 and 9) reported relatively low values of 0.50, 0.63 and 1.58 µg/g respectively and two laboratories (11 and 37) reported intermediate values of 5.27 and 8.9 µg/g respectively. In general the results appear to reflect the oxidation technique used in the methods of analysis, ie high values were associated with a dry ashing procedure whereas some wet digestion procedures produced relatively low values (Table 8). Five laboratories (41, 2, 31, 39 and 4), however, using wet digestion procedures, produced values of 13.6, 15.5, 15.7, 17 and 20.7 µg/g respectively. The differences in overall procedure between three of those laboratories (2, 4 and 31) and

laboratories 12, 8 and 9, which also used a wet digestion procedure, appears to be quite marked (Table 8). Laboratories 2 and 4 added a quantity of nickel salts to their final digest prior to measurement in the furnace and Laboratory 31 used a much stronger concentration of sodium borohydride in the arsine generation stage. The methods used by Laboratories 12 and 9 and to a lesser extent those used by Laboratories 11 and 37 would appear to suffer from matrix interferences. In an attempt to check on the true value of arsenic in Sample A the author submitted the sample to the Atomic Energy Research Establishment (AERE), Harwell, England, for analysis by neutron activation. The results of the analyses of six replicates are given in Table 7. The mean value of 15.0 µg/g (with a coefficient of variation of 6%) reported by AERE, Harwell, appears to support the relatively high values reported by Laboratories 17, 35, 41, 19, 2, 31, 20, 39, 21, 23 and 4.

A multiple range test was carried out on the data submitted by these laboratories. The results of this test are given below:

Lab. No.	17	35	41	19	2	31	20	39	21	23	4
Mean value	12.2	12.9	13.5	14.0	15.5	15.7	16.2	17.0	18.8	20.2	20.7

(KEY: Any two or more mean values underlined by the same line are not significantly different.)

The overall coefficient of variation for these eleven laboratories is 8.6%.

Cadmium

Thirty-five laboratories reported data for this metal; mean values ranged from 0.005 - 0.99 µg/g (Table 9). Two laboratories (12 and 38) reported very low values of 0.005 µg/g and 0.008 µg/g respectively and four laboratories (33, 14, 10 and 27) reported very high values of 0.28, 0.32, 0.39, and 0.99 µg/g respectively. The remaining twenty-nine laboratories reported mean values in the range 0.012 - <0.140 µg/g. The large differences in within-laboratory variability make it impossible to carry out a reliable analysis of variance to test differences between the mean values reported by the twenty-nine laboratories.

Two basic techniques were used to assess the concentration of this metal in Sample A - atomic absorption (flame and flameless) and anodic stripping voltametry (ASV). The results of these analyses indicate that the true concentration of cadmium in the sample is very close to the limit of detection of both techniques. At low concentrations of cadmium the matrix of the sample will affect the accuracy of the determination so it is essential that the metal should be separated from the matrix to remove this source of interference. Unfortunately the majority of analysts relied on the technique of 'standard addition' to overcome these interferences rather than employing an extraction procedure to isolate the metal. Only four laboratories (4, 12, 13 and

24) used an extraction procedure (either APDC/MIBK or dithizone/toluene) to isolate the metals from the digest. Laboratory 4 sprayed the extract directly into the flame; Laboratory 24 digested the organic extract with nitric acid and then injected an aqueous phase into the furnace whereas Laboratories 12 and 13 back-extracted the metals into an aqueous solution prior to injection into the furnace. Despite these procedures the results reported by Laboratories 13 and 24 are little different from the rest of the results. Apart from the analytical procedure used by Laboratory 12 one clue to the very low result (0.005 µg/g) it reported may be found in the overall approach to trace metal measurements which this particular laboratory adopts, ie all digestions, extractions and transfer procedures are carried out in a clean cabinet in which there is a positive and outward flow of filtered air. At this low level of cadmium the contamination from atmospheric particles, particularly in laboratories situated in an industrial environment, may be quite significant. It is worth noting that the mean values reported by Laboratories 6 and 21, which used ASV procedures, are some of the lowest results reported in this exercise. However, none of the analysts employing ASV procedures seem to have used a clean air cabinet for either the actual measurement step or for the steps in the procedure leading up to this part of the analysis.

Chromium

Only nine laboratories reported data for this metal; mean values ranged from 0.07 - <1 µg/g (Table 10). Three laboratories (3, 37 and 1) produced similar mean values (0.14, 0.15 and 0.18 µg/g) with respective coefficients of variation (25, 29 and 4).

Cobalt

Only four laboratories (8, 12, 22 and 34) reported data for this metal. Laboratories 8, 34 and 22 reported mean values of <0.05, <0.2 and <0.3 µg/g respectively whereas Laboratory 12 reported a mean value of 0.007 µg/g, with a coefficient of variation of 14%, based on an analysis of eleven replicates (0.006 - 0.010 µg/g).

Copper

Thirty-five laboratories reported data for this metal; mean values ranged from <0.4 - 4.0 µg/g (Table 11).

A multiple range test was conducted on data which exhibited an acceptable coefficient of variation, ie ≤20%. The results of this test, which are displayed in Figure 1, show no clear grouping of mean values except in the case of Laboratories 17 and 38, which have mean values significantly lower than the others while not themselves differing significantly, and Laboratory 40 which has a mean value significantly higher than the others. The overall coefficient of variation for the laboratories included in the multiple range test is 8%.

Iron

Fourteen laboratories reported data for this metal; mean values ranged from 5.7 - 15.6 µg/g (Table 12). Laboratory 22 reported a single value of 13.9 µg/g which appeared to be in agreement with Laboratories 32, 6, 33, 21, 1, 27 and 8 which reported values of 12.2, 12.7, 12.8, 13, 13.3, 15.5 and 15.6 µg/g respectively. The means of 15.5 and 15.6 µg/g are significantly higher than the other five values which themselves are not significantly different. The other seven laboratories (20, 23,

26 (2), 24, 26 (1), 10 and 37) reported mean values in the range 5.7 - 10.6 µg/g and here statistically significant differences were found among these mean values.

Lead

Thirty two laboratories reported results for this metal; mean values ranged from 0.018 - 7.5 µg/g (Table 13). As in previous exercises the results for lead were found to be extremely variable. Three laboratories (15, 38 and 12) reported mean values of 0.018, 0.025 and 0.028 µg/g which were about an order of magnitude lower than the majority of the values. Two very high values of 2.8 and 7.5 µg/g were reported by Laboratories 33 and 27 respectively. A group of seven laboratories (6, 30, 29, 13, 9, 26 (2) and 7) produced mean values which are not significantly different.

Manganese

Fourteen laboratories reported results for this metal; mean values ranged from 0.54 to 11.7 µg/g (Table 14). The majority of laboratories reported results with a high degree of reproducibility ie ≤ 8%, the exceptions being Laboratories 10, 32, 23, 20 and 37 with coefficients of variation of 15%, 17%, 19%, 27% and 75% respectively.

Mercury

Sample A

Thirty two laboratories reported results for this metal; mean values ranged from 0.047 - 0.37 µg/g (Table 15). Laboratory 3 reported four individual values which were so dissimilar (0.04, 0.27, 0.34 and 0.72 µg/g) that they were excluded from the statistical analysis. Laboratory 25 reported results which were considerably lower than the other laboratories and so they were not included in the multiple range test. The results of the multiple range test are presented in Figure 1. The test clearly shows that the majority of laboratories (twenty one out of a total of twenty nine) produced comparable results for the analysis of mercury. The overall coefficient of variation for the laboratories included in the multiple range test is 25%.

Sample B

Thirty three laboratories reported results for mercury; mean values ranged from < 0.01 to 0.250 µg/g (Table 16). Laboratories 8 and 4 reported values below their respective detection limits. Laboratory 22 reported a figure of 0.052 µg/g based on one analysis. The data reported by Laboratories 1, 3, 5, 16, 18, 23 and 41 were excluded from the multiple range test due to either their relatively high within laboratory variability, ie coefficient of variation > 20% or because their mean values were extremely high.

The results of the multiple range test carried out on the remaining twenty one laboratories are presented in Figure 1. The test shows that significant differences exist between some of these laboratories but that within certain groups of laboratories no significant differences can be found. The biggest of these groups consists of seven laboratories (38, 29, 12, 31, 7, 19 and 6). The overall coefficient of variation for the twenty one laboratories included in the multiple range test is surprisingly good, ie 12%.

Nickel

Five laboratories reported results for this metal. Laboratories 8, 34, 32 and 33 reported mean values of <0.05, <0.06, <0.2 and <0.6 µg/g respectively, while Laboratory 22 reported a single value of 0.19 µg/g.

Selenium

Eight laboratories reported results for this metal; mean values ranged from 0.95 to <25 µg/g (Table 17). With the exceptions of Laboratory 22, which reported a value of <0.25 µg/g, the laboratories (9, 4, 20, 41, 39, 2 and 23) appear to have produced reasonably comparable data, ie 0.95, 1.5, 1.5, 1.70, 1.72, 1.82 and 2.21 µg/g respectively.

Silver

Two laboratories reported results for this metal. Laboratory 22 reported a single value of <0.5 µg/g while Laboratory 12 reported a mean value of 0.003 µg/g with a coefficient of variation of 20%.

Vanadium

Three laboratories (32, 3 and 22) reported mean values of <0.5, <2 and <2 µg/g respectively.

Zinc

Only six of the forty one laboratories participating in this exercise did not report results for this metal. The mean values reported by the thirty five laboratories fall in the range 12.8 to 37.3 µg/g (Table 18). In all cases but three the within laboratory variability was very low; coefficients of variation fell in the range 1-10%. Laboratory 29, with its unusually high coefficient of variation (21%) was excluded from the multiple range test.

The results of the multiple range test are presented in Figure 1. The test shows that there are significant differences between groups of laboratories although within certain groups there are no significant differences. The overall coefficient of variation for the laboratories included in the multiple range test is 7%.

DISCUSSION

Forty one laboratories out of a total of fifty six which received samples 'A' and 'B' reported analytical data for some or all of the metals under examination. Unlike previous ICES exercises all of the eighteen ICES countries were represented.

On the basis of the results reported by individual laboratories for copper, zinc and mercury in Sample 'A', it seems reasonable to conclude that the majority of participants are not only reporting comparable data, but also accurate data, for these metals at their respective concentrations. In view of the large number of participants and the low concentrations of these metals in Sample 'A' these results are very encouraging. The results of the analyses of mercury in Sample 'B' are also extremely good, bearing in mind the very low level of mercury in this sample. Of the thirty three laboratories that reported results for Sample 'B', twenty two produced values of mercury in the range 0.019 - 0.062 µg/g. To the best of our knowledge no other intercomparison exercise for mercury has produced such good agreement at this level in biological tissue.

Although the return of data for arsenic analyses was poor, the results were most interesting from an analytical viewpoint. The results from an independent laboratory, employing neutron activiation analysis, suggest that the likely concentration of arsenic in Sample 'A' is ca. 15 µg/g. A number of laboratories reported mean values which were one half to one thirtieth of this value. It would appear that some of the analytical procedures used in this exercise (Table 8) may suffer from a major interference problem. The errors in the analysis of arsenic appear to be related to the procedure used for the destruction of the organic matter in the fish tissue, ie some component of the matrix, which is destroyed (or eliminated) during dry ashing but not during wet digestion, depresses the release of arsenic as arsine and also suppresses the arsenic signal in flameless atomic absorption (unless nickel salts are added to the digest prior to injection into the graphite furnace). The observations and findings suggest that some laboratories should re-examine their procedures for the analyses of arsenic in fish tissue.

As in previous ICES intercomparison exercises the comparability of results for cadmium and lead is relatively poor. Some of the reasons for this poor performance have already been discussed. It should be noted, however, that the levels of cadmium and lead in Sample 'A' are the lowest used by ICES to date, and are one to two orders of magnitude lower than those encountered in other international intercomparison studies. The outcome might have been completely different had a reference sample containing 0.1 µg/g Cd and 1.0 µg/g Pb been circulated, instead of Sample 'A' which appears to contain 0.00X µg/g Cd and 0.0X µg/g Pb. This view stems from the fact that despite the relatively poor performance in this exercise there is evidence to suggest that analysts have continued to improve their analytical methods for Pb and Cd since the last ICES exercise. The pursuit of accurate and comparable data at very low levels of Cd and Pb is obviously very desirable. From the point of view of health studies the difference between reporting results of <0.01 µg/g Cd and ca. 0.002 µg/g Cd can be highly significant, because it is common practice to ignore < signs when calculating the intake of cadmium by food and drink, and this could lead to an overestimation of the intake of cadmium if in fact the true level of cadmium was nearer to 0.001 µg/g than 0.01 µg/g. From a marine monitoring standpoint it may well be that one does not need such accurate data at these concentrations. If one is merely interested in identifying large differences in concentration of these metals in fish in space and time then we believe most of the laboratories can cope with this task with their present analytical capability. If, however, it is necessary to observe significant changes of <100% over a large geographic area with time, most of the participants need to improve their capability. One alternative to this latter approach might be to invite a small number of laboratories with proven ability to do this work on behalf of the rest of the laboratories. Future marine monitoring programmes for cadmium will no doubt centre on shellfish, since these organisms contain some of the highest and most variable concentration of this metal. The levels normally encountered in shellfish lie in the range 1 - 10 µg/g. On the basis of the results obtained in this intercomparison exercise it is highly probable that all participants will produce comparable and accurate data in this concentration range. The recent IAEA intercomparison exercise, using samples based on a sea plant and copepods, suggest that even at levels of 1 µg/g some laboratories do not report accurate data for cadmium. In view of the findings of this exercise (IAEA, 1978) it has been agreed that ICES should conduct another comparison study for cadmium, at a concentration in the range 0.1 - 1.0 µg/g. It has also been agreed that ICES should organise a further exercise for lead at the same time, at a concentration in the range 1 - 10 µg/g.

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PART II - ORGANOCHLORINES

INTRODUCTION

Earlier intercalibration exercises for organochlorine residue analysis were carried out, using a spiked fish oil, in 1972, and in 1974 using a spiked corn oil. The results were given in detail in an earlier report (ICES Cooperative Research Report, No.80). The residue levels in the fish oil were considered to be too high by the analysts who participated, and did not constitute a sufficient test of their ability to determine residues at levels more commonly encountered in marine fish. To provide a base oil reasonably free of organochlorine residues, enabling lower concentrations of selected organochlorines to be added as spikes, the corn oil was chosen for the 1974 exercise but this was subsequently criticised as being easier to analyse, and too different from the usual types of fish extract obtained by analysts from marine fish. In May 1977 the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic proposed that, for a further intercalibration programme, an unspiked fish oil containing undisclosed amounts of organochlorines should again be circulated, and also three different mixtures of organochlorine residues for which the concentrations would be stated. The Pitlochry Laboratory of the Department of Agriculture and Fisheries for Scotland, which had been responsible for the preparation and distribution of earlier samples, was asked to undertake this new exercise.

Nine different samples of fish oil were obtained from the Marfleet Refining Company Ltd. of Hull, England, and were analysed for organochlorine residues (Table 20). From this series a capelin oil of low residue content was selected for the intercalibration exercise (the capelin were caught off Iceland), and a larger consignment of the same type of oil was acquired, from which aliquots were taken for distribution to the participants.

Before the various standard solutions were prepared, enquiries were made of the airline and postal authorities regarding transport of inflammable liquids. It was confirmed that these authorities will not permit the carriage of inflammable solvents except in certain circumstances, and the proposal to distribute standard mixtures in n-hexane had to be abandoned. Suggestions were later made by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic in May 1978 that standards could be made up in mineral or silicone oil but, apart from the difficulty in preparing such solutions without the aid of normal solvents, it was considered that the oils could interfere with the adsorption column chromatography commonly used for clean-up and separation purposes. The preparation of accurate standards for distribution is also time-consuming and costly, and the Pitlochry Laboratory was not able to allocate funds for the work, while it was not possible for ICES to defray the expenditure incurred. Furthermore, it was considered by the Pitlochry Laboratory that competent analysts should be able to prepare their own standards in pure solvents with sufficient accuracy, and the proposal to distribute standard mixtures was given up. A letter was circulated in July to nineteen laboratories giving the name and address of a source of standard pesticides of high purity. This was unfortunately not sent to latecomers in the exercise, but in any case very few recipients seem to have taken advantage of this information.

In previous exercises, to prepare a spiked sample for distribution, carefully measured quantities of individual organochlorines in small volumes of solvent had been mixed thoroughly into a part of the accurately measured final volume of the matrix oil, and this portion of the oil subsequently added to the remainder and again mixed thoroughly for several hours. The spiked and unspiked oils were then analysed repeatedly with great care, to confirm that the measured spike concentration for each residue was in general agreement with the amount added. This procedure can be time-consuming and costly, and in view of the pressure of other commitments the Pitlochry Laboratory had to abandon the preparation of a spiked version of the selected fish oil.

DISTRIBUTION OF SAMPLES

A letter from the General Secretary of ICES was circulated to all Delegates in April 1978, informing them of the proposed intercalibration exercise, and by the end of August 1978 a total of 24 laboratories had been notified to the author at Pitlochry as being willing to participate. Samples of the selected fish oil were despatched to these laboratories on 21 August 1978. At that time, no laboratories in Canada, France, Spain, USSR or Poland had been named, and the General Secretary was informed. He issued a further intimation to the Delegates of these countries on 1 September 1978, and laboratories in Canada, France, Spain and Poland subsequently requested samples. By 6 November 1978, 43 samples had been despatched but no results had been received from any laboratory. At this time the closing date for receipt of analyses was fixed at 31 January 1979. (See Table 19 for list of laboratories.)

All the recipients of the sample were asked to provide information on their analytical techniques, examples of the chromatograms of standards and sample analyses, and of a concentrate of the solvent used. The appropriate detection limits for 10 different residues were indicated, but analysts were invited to determine as many organochlorine residues as they could (Appendix IV).

By 22 December 1978 only 7 sets of analyses had been reported, and by 17 January 1979 only 10 had been received. The first deadline of 31 January 1979 passed with only 12 sets of results from a total of over

40 laboratories, many having had the samples for 5 months. The names of several laboratories were provided by the Joint Monitoring Group of the Oslo and Paris Commissions in January 1979, but only two of these (Nos. 10 and 11 in Table 19 had not already been sent samples of the fish oil, and these samples were despatched on 29 January 1979. Both laboratories replied within 6 weeks reporting their results, indicating that the analysis could be completed within a relatively short time.

Up to the end of March 1979 only 19 laboratories had submitted their results. One laboratory (No. 27) had used 2 separate samples of oil, having received 1 from an associated national laboratory. A second laboratory (No. 16) used 2 separate groups of analysts to analyse the sample. The total time between sample despatch and receipt of the analyses had varied at this time (among 19 laboratories) from 5 to 29 weeks, with an average of 16 weeks.

This response was considered to have been very disappointing, in view of the fact that a high proportion of the recipients of the sample were known to have considerable experience of organochlorine analysis in fish. An interim report on the results received up to the end of March 1979 was prepared and presented to the Marine Chemistry Working Group in Lisbon in May 1979, and it was indicated that the coefficients of variation from the residues reported by most analysts were similar to those from the previous unspiked fish oil sample used for inter-calibration in 1972.

Further results were received from 10 laboratories by the end of June, and this report presents the entire series of results. None of the later analysts had received a copy of the interim report before their results were despatched to the author. A further laboratory, which had encountered difficulty with the analysis due to the possible presence of toxaphene in the sample, submitted its results later but these too have been included in this final report.

It was thought probable that several laboratories had attempted to identify and quantify some substances which they would have ignored in the course of their routine work, but these results are not self-evident from the reports received. A total of 21 different residues or residue groups was reported from the ICES laboratories, 8 of them by more than half of the laboratories. Single values were given for TCNB, endosulfan, heptachlor, op-DDE, α- and β-chlordane, two for endrin and toxaphene, 3 for op-TDE, pentachlorobenzene and β-HCH, and 5 hepta-chlorepoxide. One laboratory also reported oxychlordane, transchlordane and transnonachlor. As no confirmatory methods were used in most cases these residues must be regarded with suspicion. Nine measured values were reported for op-DDT, while 15 were given for δ-HCH and 16 for dieldrin. HCB, DDE, TDE, DDT and PCB were measured by from 21 to 25 laboratories.

Two laboratories reported the presence of toxaphene. This pesticide is thought to be used only to a limited extent in western Europe, and it seems unlikely that fish off Iceland could be significantly con-taminated by it. The distributing laboratory at Pitlochry has never detected the presence of toxaphene in any marine samples in the North Sea or eastern North Atlantic, but subsequently confirmed peaks corresponding to toxaphene in the capelin oil by the use of GCMS. The concentrations reported in the sample (1-5 mg/kg) were higher than the combined total of all other organochlorine residues, which also suggests an unlikely level of discharge to the marine environment in the region of Iceland. All the laboratories reporting toxaphene are very

experienced, however, and the suggestion that this pesticide was present in the sample requires further consideration.

One laboratory reported only on PCB, a faulty gas chromatograph being given as the reason for a failure to measure other residues. One JMG laboratory also reported only on PCB, although this was all that had been asked of the JMG group. A few laboratories identified only 2-5 residues, but on the other hand 15 laboratories measured at least 8 different residues, excluding those reported to be below the limit of detection. The complete series of analyses reported is presented in Table 21.

STATISTICAL ANALYSIS OF RESULTS

The preliminary analysis of the data obtained by 31 March 1979 indicated that there were wide variations in the reported concentrations of some of the residues and many analysts had indicated that they had had difficulty in performing the analysis, although the capelin oil used had been extracted from fish taken in a relatively clean area of the ocean. Following the receipt of further analytical data from a number of laboratories, additional information on the analytical methods used and examples of chromatograms were requested. It was clear, as the result of an examination of this information, that a wide variety of methods had been used for preparation of the organochlorine extracts before analysis by GLC, and some of these may have influenced the analysis. The quality of the chromatograms was also very variable, ranging from the high resolution of some capillary columns to poor resolution by packed columns in a few instances. Examples are given in Appendix V.

In view of the possibility that the quality and accuracy of the final analyses might be dependent upon either the high resolution of the capillary columns (which might not require separation of residues prior to GLC analysis), or the method of treatment of the extract or of residue separation before GLC injection, the data were separated into four groups before variance analysis. These comprised six sets of data from capillary columns, six from analysts using normal GLC columns but only sulphuric acid treatment for clean-up, and two groups from analysts using absorption columns for clean-up and a preliminary separation of residues prior to analysis by GLC. The two groups comprised the results from chromatograms judged by inspection to be of higher quality (mainly due to better peak separation) and the results from a series of chromatograms which were of noticeably lower quality, sometimes showing evidence of inadequate clean-up. However, statistical analysis of the results from these groups did not reveal any clear distinction between them in respect of the mean values of the residues reported, and the results given in this report are from the combined group of analysts using pre-GLC separation and packed GLC columns.

Values for the concentrations of the eight different residues most commonly reported (including PCB as one determination) were available for statistical analysis, although sulphuric acid treatment destroys dieldrin and values for δ-HCH were often not given, or were below the detection limit. The results of the chemical analyses in each group are shown in Tables 22-24, and the means and coefficients of variation between analysts for each residue in Table 25. Residue concentrations differing from the mean by more than three standard deviations have been excluded from the calculations. Mean values of the concentrations found in two separate samples by Laboratory No. 27 have been used in the statistical analysis, but results from two separate methods given by each of Laboratories 7 and 16 have been used individually.

Despite the wide variation in analytical techniques there is reasonable agreement between the mean values in the groups for most of the residues determined. No statistically significant differences between the means by the different methods were found at the 5% level for HCB, α-HCH, δ-HCH, dieldrin, DDE, TDE, or DDT, although this is largely due to the variance between the values reported within each of the three analytical groups. The mean values for PCB by the sulphuric acid clean-up method, however, were significantly higher than those obtained by the other methods. In the initial comparison, the six laboratories selected from the total using sulphuric acid were those not using capillary columns or any other pre-GLC separation process. To test whether the larger group of laboratories using sulphuric acid had produced results differing from those of other laboratories, irrespective of the form of GLC used or other preparatory processes, data from all thirteen laboratories using sulphuric acid were pooled (Table 23).

The sulphuric acid technique, which is used to destroy interfering material in solvent extracts of organochlorines, also destroys dieldrin, but may possibly introduce substances which could be electron-capturing. Thus there may be an increase in the number of GLC peaks on the chromatograms by comparison with those from non-destructive techniques. An increase in the number of peaks could lead to a greater chance of interference with the peaks from substances originally present, or an increased risk of peaks which could be incorrectly identified. Some of the thirteen laboratories in this group from which analytical data were used in the final statistical analysis employed alkaline hydrolysis or chromic acid treatment of an aliquot of the extract in the determination of pp-DDT group residues, thus making allowance for possible interference by PCB peaks.

The high mean value for the PCB residues reported by the group of analysts using sulphuric acid does not appear to be explained by interference with other residues. The peaks of TDE and DDT can sometimes be separated from the major PCB peaks on a good GLC column, but the use of alkaline hydrolysis prior to PCB quantification will remove any interference by these substances. One laboratory (No. 7) used both alkaline hydrolysis and chromic acid on an aliquot of the fish oil extract which had received sulphuric acid treatment, while a second aliquot was separated on a silica gel TLC plate as an alternative method of analysis. The latter method gave a significantly lower value for the PCB concentration ($p<0.10$). It is also worth noting that one laboratory (No. 1) determined the PCBs by perchlorination to decachlorobiphenyl after sulphuric acid treatment.

Of the thirteen laboratories in this group, seven reported values over 1000 µg/kg, but only one of four using capillary columns did so (No. 31). Of the six reporting values below 1000 µg/kg (190 - 750 µg/kg) three used capillary columns (Nos. 10, 32, 34), one (No. 23) had experienced difficulty with the sensitivity of the chromatograph and No. 35 used a more elaborate procedure for separating the PCB residues than was generally employed. Among the thirteen laboratories using alternative clean-up techniques (Table 24) only two reported PCB values over 1000 µg/kg (Nos. 3 and 28). Laboratory No. 3 used a 1:1 mixture of Aroclor 1254 and 1260 for reference, but was not confident of the accuracy of the PCB value determined, believing it to be probably between 0.9 and 2.5 µg/kg.

Only the mean of the PCB values determined by use of the sulphuric acid technique differed significantly from that using other techniques. The means of the other six residues (excluding dieldrin, which was not determined with the use of sulphuric acid), were not distinguishable statistically between the methods. The use of different reference formulations for PCBs, or different numbers of peaks, in calculating the PCB content could not be shown to influence the PCB value significantly. One other high value of 8000 µg/kg PCB was reported, by Laboratory No. 13,

which determined only HCB, α-HCH and PCB. Clean-up was by silica column, with no further residue separation. This value would have been excluded from the statistical analysis as lying well outside the ± 3 sd range, had the laboratory been one of those using the analytical techniques considered in Tables 22-24.

A number of laboratories used packed columns but no pre-GLC residue separation, but most of them also employed sulphuric acid as a clean-up procedure. Consequently the statistical analysis of the results obtained by this group (Table 26) yielded mean values of the most commonly reported residues which were not significantly different from those in the sulphuric acid group. However, comparison with the results from the group using other forms of clean-up and pre-GLC separation (Table 24) showed that the means for DDT were different ($0.05>p>0.01$), as well as the means for PCB ($p<0.01$). The latter difference has already been noted for the analysts using sulphuric acid clean-up. The numbers of laboratories in these groups are inevitably small, and not every laboratory was able to report on every residue subjected to the statistical analysis, so that deductions from this analysis must be made with caution. Of the compounds under consideration, the major interferences between residues, if no pre-GLC separation is undertaken, are those between the PCB group and the DDT group. DDE often exceeds the interfering PCB peak considerably, and the error for this substance will in such circumstances be small. However, pp'-TDE and pp'-DDT may be more significantly affected, but of the laboratories in Table 25 determining these residues all but one used an alkaline reaction to remove the TDE and DDT, thus giving a means of estimating the size of interfering PCB peaks and correcting for this interference.

The use of high resolution capillary or WCOT columns for the gas chromatographic analysis should make the use of pre-GLC residue separation unnecessary. However, there is a possibility that the large number of peaks resolved on a capillary column, especially if temperature-programmed, may lead to confusion regarding the identity of individual peaks. The timing of peak elution is critical, and is normally achieved by automatic timers, but care is clearly necessary to maintain uniform temperature and gas flow conditions, which could otherwise cause serious errors in peak identification from automatic recognition systems based on elution time. One laboratory, using a temperature-programmed capillary column, submitted chromatograms showing 65-70 peaks following acid treatment of the extract from the ICES sample, while the same extract divided (without pre-treatment by sulphuric acid) on a silica column into two fractions produced a total of about 150 peaks, of which over 50 would be easily measurable (more than 5% fsd). (Some compounds may have appeared in both fractions.) Although incorrect peak identification may lead to errors in quantification in some instances, it is unlikely to provide the explanation for the generally higher concentrations of PCBs reported following the use of sulphuric acid as a clean-up procedure.

The data from the groups of analyses between which no significant differences could be detected have been combined in Table 27. It will be seen that the coefficients of variation between laboratories for the various residues lie between 32% and 71%. As recorded earlier, many analysts found difficulty in analysing the fish oil, and commented that the chromatograms were not within their usual experiences. In the view of the distributing laboratory, however, samples of clupeoid fish, or of the liver of gadoids, both of which contained relatively high levels of lipid, frequently yield chromatograms of a quality similar to that of the intercalibration sample.

The largest coefficient of variation found was for δ-HCH (71.1%), but the mean of the concentrations reported, 11 µg/kg, was the lowest of the

eight residues studied in the statistical analysis. Five of the twenty laboratories reporting on this substance could only state that the concentration was below their level of detection, and one reported an abnormally high value. For residue concentrations in the range 50-100 µg/kg (or 500-1000 µg/kg for a mixture of PCBs), the coefficients of variation found were 33 - 50%, which indicates that 19 out of 20 analysts obtained values for most of the residues which spanned at least an order of magnitude. This cannot be considered a satisfactory measure of agreement among a group of laboratories many of which have been engaged in organochlorine analysis for a number of years. One possible means of improvement could lie in the wider use of capillary columns to improve separation and identification. It is perhaps significant that in Table 25 most of the determinations using this method showed the smallest coefficients of variation.

In 1972 a fish oil was also used as a basis for preparing an intercalibration sample (No. 2A), spikes of several organochlorine compounds being added to it (No. 2B). Residue concentrations found in the unspiked oil were higher than in the capelin oil used in the latest exercise (Sample No.4), but the coefficients of variation for the residues found were generally within the same range (Table 28). The much higher spike concentrations added to the oil in the 1972 exercise produced better agreement among analysts, as did the lower spike concentrations added to an uncontaminated (essentially residue-free) corn oil in 1975. This supports the view that estimating spike concentrations (by difference from the matrix), or at least higher concentrations, results in a higher level of agreement (lower coefficient of variation) than the determination of low concentrations in natural fish oils. This in turn suggests that agreement among analysts on the residues found in a natural sample containing very low concentrations, as in a fish tissue of low lipid content, would be even poorer. Unfortunately such samples tend to give rise to many returns from analysts in which residues are only indicated as being present at less than the limit of detection, information not amenable to subsequent statistical treatment.

METHODS OF CHEMICAL ANALYSIS

Appendix VI gives details of the analytical procedures used by the participants. A few laboratories used more than one preparatory technique, but several used more than one GLC column. Six laboratories used wall-coated or capillary GLC columns (one using two different types). In the other 24 laboratories 35 packed columns were employed with a wide variety of packing, although most columns were 1.5 - 2.0 m in length.

The extraction/solution stage involved the use of hexane or petroleum ether in 22 instances, pentane in three and dichloromethane or cyclohexane each in one laboratory. In four instances mixtures of solvents were employed, toluene/ethyl acetate in one, acetone/hexane in one and acetone/acetonitrile/hexane in two cases.

Clean-up of the oil extract or solution was carried out by a variety of methods. In 13 laboratories sulphuric acid was used, and alumina columns in eleven. Other methods used were liquid/liquid partition (2), Florisil columns (3), silica on TLC plates or columns (2), saponification (1) and gel permeation (1).

Pre-GLC residue separation was made on Florisil columns in five laboratories and by silica columns or TLC plates in fifteen.

The GLC stage was temperature-programmed in seven instances, from a total of 42 columns, and automatic integration of peaks used by seven laboratories.

Confirmation by GCMS, for at least some of the residues, was used in five laboratories, PCB confirmation and quantification by perchlorination in two, and chemical reaction of DDT group residues (chromic oxide, alkaline hydrolysis and a magnesium oxide micro-reactor as a GLC pre-column) in nine laboratories.

Solvent purity, as judged by chromatograms after usually one hundredfold concentration, was in most cases very good, and only in one or two cases were peaks in the solvent likely to interfere with residues in the sample.

The quality of the chromatograms submitted was very variable. Estimates of the resolution of the GLC columns were made by calculating the number of theoretical plates for a dieldrin or DDE peak and, excluding the capillary columns, values ranged from 800 to 4000 on columns of 1.5 - 2 m in length. More than half of the columns used gave values of more than 2000 plates, and about 1/3 exceeded 3000 plates. However, comparison of chromatograms of standard mixtures with those from sample extracts showed in many instances that the baseline of the latter samples was markedly non-linear, making quantification of peak height or area difficult. The sensitivity available (or used) in some instances was inadequate to detect more than a few peaks, while in other cases a large number of unidentified peaks were present in the pesticide fraction after removal of PCBs. Laboratories not using pre-GLC separation techniques were more liable to have mis-interpreted the identity of peaks, or to have incurred errors in quantification due to interference of one residue by another.

SOURCES OF VARIATION

The extent of variation between analysts is shown by the ranges of values reported for the residues most commonly determined, as summarised below.

HCB	40 - 116 µg/kg
α-HCH	1 - 131
ϑ-HCH	2 - 136
Dieldrin	12 - 129
pp'-DDE	16 - 340
pp'-TDE	5 - 180
pp'-DDT	30 - 305
PCB	190 - 8000

These ranges cover one and in some instances two orders of magnitude, but in the latter case elimination of one outlier will reduce the range to about one order of magnitude. Nevertheless even this degree of variation between laboratories suggests that there is room for considerable improvement, and some possible sources of error can be considered.

The samples distributed, which can be considered to be homogeneous aliquots from a large volume of oil, should have given no problems in obtaining an extract of all organochlorine residues, unlike fish tissue samples which require an extraction stage. The latter itself could provide a source of variance in the analysis of samples for routine monitoring, but this should have been absent in the exercise under discussion.

All solutions of the fish oil required a clean-up stage to remove lipids and pigments which otherwise interfere in the GLC analysis. Serious interference is revealed by unstable or wandering recorder baselines, and in some cases these were present in the chromatograms submitted. If the cleaned-up extract is further processed to obtain two or more fractions containing different groups of residues, that containing PCBs (normally the first to elute from an adsorbent column) will be relatively free of interfering substances (lipids, co-extractives). Subsequent fractions may contain significant amounts, particularly if the lipid loading on an adsorbent column is excessive, and the baseline of the chromatogram may be unstable. If sulphuric acid is used for the clean-up stage, some reaction products from the destruction of lipids and other co-extractives may remain and interfere in the chromatograms.

In view of the large number of individual compounds which are likely to have been present in the sample, good separation of the individual GLC peaks is essential. This was achieved by most of the analysts who used capillary columns without the need to subdivide the extract into fractions before GLC injection, although there was some variation in the quality of chromatograms even using capillary GC. One laboratory used silica columns to separate the residues before GLC on a wall-coated open tube (WCOT) and achieved good separation of residues (these results were included with capillary column results for the purpose of statistical analysis).

Where capillary or WCOT columns were not used, pre-GLC separation or residues was essential for satisfactory separation on GLC columns. Chromatograms of single cleaned-up extracts containing all residues generally suggested that there was some confusion of identity of the peaks, particularly between PCB peaks and those of pesticides. Separation was usually made on silica columns, which were more effective than Florisil for this purpose.

The sensitivity of the GLC detector was inadequate, in many instances, for the purpose of obtaining peaks large enough for accurate measurement of peak heights and higher concentrations of the residues could have been obtained by, for example, evaporating an eluate to a smaller volume. Approximately one third of the laboratories produced chromatograms which demonstrated effective peak separation with adequate peak heights. Half were from capillary columns, and of the others none had been produced from sulphuric acid clean-up.

Chemical reaction was used in a few instances for confirmation of DDT group residues, mostly when no pre-GLC separation had been made. The DDT and TDE residues were estimated by difference following alkaline hydrolysis, and two analysts used chromic oxide to remove DDE for the same purpose. In all cases PCBs are likely to be the interfering peaks. The difference based on peak area calculation is more accurate than that from peak height unless the retention times of the interfering peaks are identical, which is rarely the case.

DISCUSSION

This exercise was much less satisfactory than previous intercomparison exercises. Analysts found the sample more difficult, primarily because the concentrations of residues in the lipid were lower than in previous samples, thus requiring more efficient clean-up. The number of residues found at the level of sensitivity used by many analysts made residue separation very important, but those who employed a lower level of sensitivity could have had difficulty in identifying many of the residues.

The long delay in submitting results to the author perhaps emphasises the problems experienced in the analysis of this sample.

The provision of chromatograms to accompany the analytical report, and the detailed description of techniques, proved particularly valuable and at the same time revealed a basic problem in assessing the analytical data. If the assessment is made without evidence of chromatogram quality, it is assumed that all data are equally reliable both in respect of the identity of residues and their concentrations. However, a study of the analytical methods often reveals that the identity of some residues must be questioned, while examination of the chromatograms suggests in many instances that both identity and concentration may be inaccurate.

All the exercises so far have given the participating analysts freedom to use techniques of their choice, in the hope that agreement between them in respect of the results reported may be found satisfactory. This latest exercise suggests that such will be the case only for samples which are relatively easy to analyse, with high concentrations of a few easily identifiable residues and no problems of clean-up. The spiked samples used in earlier exercises were examples. At low residue levels, for which extracts must be concentrated in order to provide measurable values of the concentrations suitable for statistical analysis, many interferences arise and good separation techniques become essential.

It is suggested that some restriction of the choice of analytical procedure may now be necessary, and that in particular either capillary GLC, or alternatively packed column GLC following preliminary residue separation, should be mandatory. Clean-up techniques may involve either sulphuric acid or adsorbent, but the latter seem to have certain advantages and more often produced good quality chromatograms in this exercise. With capillary columns, however, sulphuric acid seems to have been very successful.

For the purpose of statistical evaluation of the data submitted, it would also be useful to have the results of replicate analyses (using the complete procedure in each case, not replicate GLC injections). However, the cost of organochlorine analysis may make this prohibitive. Duplicate analyses are insufficient, unless the data for different residues are pooled and the variance for each assumed to be the same. Five or six complete analyses would be preferable, but in view of the time required for such a series it is likely that few laboratories would be prepared to undertake the work.

Calculations of residue concentrations have been based mostly on peak height measurements although a few laboratories have used integrators. With simple chromatograms these instruments should be very accurate but where peak overlaps are common, or small peaks appear on the edge of larger peaks, and where baselines are erratic, the accuracy may be less certain. Peak identification is sometimes made by computer from reference data, but variation in temperature may cause changes in elution time and consequent errors in identification.

PCB concentrations have been determined in this exercise by peak height using from one to 24 peaks, peak area, the use of individual isomers, one or mixed formulations as reference standards, and perchlorination to decachlorobiphenyl. It was not possible to identify any method as being of less accuracy than others, although in view of the difference between the composition of the PCB mixture in the sample and in standards it would seem desirable to use at least three of the larger peaks which did not interfere with other known residues. On capillary columns, a larger number of individual peaks can be used with greater freedom of interference. Once again, in any future exercise certain requirements could be specified in respect of PCB calculations.

The sample circulated for this exercise has been criticised as being more difficult to analyse than material normally dealt with by the participating laboratories, although earlier intercalibration samples were thought to have been too easy and atypical. In one respect the capelin oil was unusual, in that the concentrations of the residues expressed on a lipid basis were probably significantly lower than those obtained on the same basis from fish sampled in any coastal waters of Europe and North America, even in ostensibly unpolluted areas. Fish tissue samples, especially if of low lipid content, will in many cases give fewer problems in clean-up, but also lower concentrations of contaminants on a fresh weight basis, the form in which most analysts would expect to express their results. Nevertheless, if analysts are to provide information on an increasing number of pollutants, with a degree of accuracy which ensures their acceptability to authorities in other countries, intercalibration exercises in the form provided by Sample No.4 are essential. It is to be hoped that by such means laboratories will identify their weaknesses, and will improve their techniques to a standard at which agreement among analysts will be much closer. Unless this is achieved, it will be difficult to accept the validity of organochlorine analyses reported by many countries for the fish and other samples taken in their own waters, or by their commercial or research vessels. Some consideration must be given to the level of agreement to be expected among analysts before the information they report on environmental concentrations can be accepted by others.

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Table 1. Laboratories which participated in 4th ICES Trace Metal Intercomparison.

Country	Institute	Lab.No.	Analyst
Belgium	Ministère de l'Agriculture Institut de Recherches Chimiques Molenstraat 5, 1980 Tervuren	1	P. Herman
Canada	Dept. of Fisheries and the Environment Technology Branch POB 429, Halifax, N.S.	2	J. Uthe
	Ministry of Agriculture and Food Provincial Pesticide Residue Testing Lab. Guelph, Ontario N19 2W1	3	H.E. Braun
France	Institut Scientifique et Technique des Pêches Maritimes Rue de I'Ile d'Yeu, BP 1049 44037 Nantes Cédex	4	Y. Thibaud
Federal Republic of Germany	Bundesforschungsanstalt für Fischerei Isotopenlaboratorium Wüstland 2, 2000 Hamburg 55	5	U. Harms
Ireland	Dept. of Fisheries Fisheries Research Centre Abbotstown, Castleknock, Co. Dublin	6	D. O'Sullivan
Netherlands	Institute for Fishery Products TNO Dokweg 37, Postbus 183 IJmuiden	7	A. Ruiter
Norway	Government Vitamin Institute Directorate of Fisheries, POB 187 N5001 Bergen	8	K. Julshamn
Scotland	Dept. of Agriculture and Fisheries for Scotland, Marine Laboratory POB 101, Victoria Road, Aberdeen AB9 8DB	9	G. Topping
USA	US Dept. of Commerce NOAA SE Utilization Research Centre Regents Drive, Maryland 20740	10	G.M. Meaburn
	US Dept. of Commerce NOAA National Marine Fisheries Service Milford Laboratory, Milford, Connecticut 06460	11	R. Greig
	Marine Research Laboratory University of Connecticut Noank, Connecticut 06340	12	S.Y. Feng

Table 2. Results of fish flour analysis (µg/g).

Laboratory Number	Lead			Cadmium		
	Mean	Standard deviation	Coeff. of variation	Mean	Standard deviation	Coeff. of variation
1	1.51	0.026	1.7	0.06	-	-
2	0.66	0.16	24.3	0.030	0.0016	5.5
3	0.68	0.26	37.8	0.058	0.0083	14.3
4[*]	0.16	0.012	7.4	0.040	0.0089	22.4
5a[**]	0.51	0.038	7.6	0.024	0.0049	20.4
5b	0.63	0.061	9.7	0.022	0.0017	7.8
6	1.24	0.30	24.3	0.058	0.011	18.2
7	0.87	0.068	7.9	0.030	0.0059	19.7
8	0.030	0.059	19.5	0.051	0.0036	7.1
9	0.66	0.073	11.1	0.048	0.0093	19.5
10	0.51	0.12	24.3	0.032	0.014	45.4
11	0.60	0.040	6.8	0.139	0.034	24.8
12	3.08	0.097	3.2	0.208	0.0003	0.1

[*] Following circulation of this report Laboratory No.4 has submitted additional analytical data for lead - 0.40, 0.64 and 0.70 µg/g; mean value of 0.58 µg/g.

[**] See Appendix II for difference between (a) and (b).

Table 3. Comparison of lead and cadmium data (µg/g) for 1975 and 1977 ICES Intercalibration Exercises.

Laboratory No.	Lead				Cadmium			
	1975		1977		1975		1977	
	Mean	C.V.*	Mean	C.V.	Mean	C.V.	Mean	C.V.
1	2.08	3.7	1.51	1.7	0.053	40.8	0.06	-
2	0.52	2.7	0.66	24.3	0.023	12.2	0.030	5.5
3	0.25	26.5	0.68	37.8	0.177	33.3	0.058	14.3
4	4.0	10.0	0.16+	7.4	0.41	12.2	0.040	22.4
5	0.53	10.5	0.51	7.6	0.028	6.4	0.024	20.4
7	0.51	16.6	0.87	7.9	0.055	21.1	0.030	19.7
8	0.81	2.5	0.30	19.7	0.042	13.3	0.051	7.1
9	0.34	20.5	0.66	11.0	<0.03	-	0.048	19.5
10	1.18	18.0	0.51	24.3	0.17	69.9	0.032	45.4
11	3.00	45.1	0.60	6.8	<0.24	-	0.139	24.8
12	2.30	2.8	3.08	3.2	0.39	12.0	0.208	0.1
Overall mean values	1.50		0.87 0.60**		0.159		0.07 0.043++	

* C.V. = Coefficient of variation

** This value has been calculated by excluding the mean values from Laboratory Nos. 1 and 12 and replacing the original data from Laboratory No.4 with the latest set of data.

+ Following circulation of this report Laboratory No.4 has submitted additional analytical data for lead - 0.40, 0.64 and 0.70 µg/g; mean value of 0.58 µg/g.

++ This value has been calculated by excluding the mean values from Laboratory Nos. 11 and 12.

Table 4. Comparison of reported detection limits (μg/g) for lead and cadmium analysis for 1975 and 1977.

Laboratory No.	Lead		Cadmium	
	1975	1977	1975	1977
1	1	0.05	0.02	0.005
2	0.02	0.001	0.005	0.005
3	0.007	0.01	0.006	0.005
4	1.5	0.1	0.05	0.02
5	0.004	(a) 0.006 (b) 0.005	0.001	(a) 0.0012 (b) 0.0004
7	0.02	0.018	0.0027	0.008
8	0.05	0.02	0.005	0.003
9	0.2	0.13	0.03	0.013
10	0.2	0.12	0.015	0.007
11	1.5	0.067	0.20	0.014
12	0.35	0.42	0.06	0.04

Table 5. Laboratories which participated in 5th ICES Trace Metal Intercomparison Exercise.

Country	Institute	Lab. No.	Analyst
Belgium	Ministère de l'Agriculture Institut de Recherches Chimiques B 1980 Tervuren, 1e Museumlaan 5.	1	J.R. Istas
Canada	Fisheries & Environment Canada Fisheries & Marine Affairs Case Postale 550, Halifax, Nova Scotia	2	G.R. Sirota
Denmark	Water Quality Institute 11 Agern Alle, DK-2970 Hørsholm	3	V.B. Jensen M. Reuss
	Ministry of the Environment National Food Institute Mørkhøj Bygade 19, DK-2860 Søborg	4	A. Andersen E.H. Larsen
	Isotopcentralen/ATV Skelbækgade 2, DK-1717 Copenhagen	5	K. Pedersen
German, Dem.Rep.	Akademie der Wissenschaften der DDR Institut für Meereskunde Warnemünde Seestrasse 15, 253 Warnemünde	6	L. Brügmann
	Hygiene-Institut Rostock Stephanstr. 18, DDR 25 Rostock	7	G. Manthey
Finland	Institute of Marine Research POB 166, 00141 Helsinki 14	8	F. Koroleff
France	Institut Scientifique et Technique des Pêches Maritimes, rue de l'Ile d'Yeu BP 1049, 44037 Nantes Cédex	9	Y. Thibaud
	Centre National pour l'Exploration des Océans, Centre Océanologique de Bretagne BP 337, 29273 Brest Cédex	10	J.L. Martin
	Laboratoire Municipal rue de Professeur Viges, 33000 Bordeaux	11	J.G. Faugere
Federal Republic of Germany	Bundesforschungsanstalt für Fischerei Isotopenlaboratorium, Wüstland 2, 2000 Hamburg 55	12	U. Harms
	Staatliches Veterinäruntersuchungsamt für Fische und Fischwaren, Schleusenstr. 2190 Cuxhaven	13	R. Kruse
	Institut für Meeresgeologie und Meeresbiologie, Senckenberg Wilhelmshaven	14	G. Irion
Iceland	Marine Research Institute Skúlagata 4, Reykjavik	15	J. Olafsson

/Cont'd.

Table 5 (Continued)

Country	Institute	Lab. No.	Analyst(s)
Iceland	Icelandic Fisheries Laboratory Skulagata 4, Reykjavik	16	S. Gisladottir
Ireland	State Laboratory Upper Mermion Street Dublin 2	17	C. Murphy
	Dept. of Fisheries Fisheries Research Centre Abbotstown, Castleknock, Co. Dublin	18	D. O'Sullivan
Netherlands	Institute for Fishery Products TNO Dokweg 37, 1976 CA IJmuiden	19	J. Luten
	Food Inspection Department Prinsegracht 50 2512 9A The Hague	20	A.J.K. Haneveld
	Government Dairy Station Vreewijkstraat 12B 2311 XH Leiden	21	L.G.M. Th. Tuinstra
Norway	Sentralinstituttet for Industriell Forskning Forskningsveien, POB 350 Blindern, Oslo 3	22	P. Paus B. Enger
	Fiskeridirektoratets Vitamininstitutt Lars Hillesgt 26, POB 187 5001 Bergen	23	K. Julshamn
	Hermetikkindustriens Kontrollinstitutt POB 329, N 4001 Stavanger	24	B. Uppstad
	Norwegian Inst. for Water Research POB 333, Blindern Oslo 3	25	H. Hovind
Poland	Institute of Meteorology & Water Management Maritime Branch, Hasryingtome 42 81-342 Gdynia	26	Ms A. Brzezinska
Portugal	CEPESA Rua Rodrigo de Fonseca 74-1°Dt° Lisbon	27	
Spain	Laboratorio Oceanografico Mar Meno POB 22, San Pedro del Pinatar Murcia	28	J. Guerrero
Sweden	Statens Naturvårdsverk Undersökningslaboratoriet 170 11 Drottningholm	29	M. Edgren
United Kingdom	Ministry of Agriculture, Fisheries and Food Remembrance Avenue, Burnham-on-Crouch Essex CM0 8HA, England	30	D. Lawson

/Cont'd.

Table 5 (Continued)

Country	Institute	Lab. No.	Analyst(s)
United Kingdom	Marine Laboratory POB 101, Aberdeen AB9 8DB Scotland	31	J.M. Pirie
	ICI Brixham Laboratory Devon, England	32	D. Taylor
	North West Water Authority Rivers Division, Warrington England	33	M. Horne
	Clyde River Purification Board East Kilbride, Scotland	34	T. Leatherland
	Marine Biological Association Plymouth, Devon England	35	G. Bryan
USA	Marine Science Institute University of Connecticut Avery Point, Groton Connecticut 06340	36	S.Y. Feng
	United States Environmental Protection Agency Environmental Research Laboratory South Ferry Road, Narragansett Rhode Island 02882	37	P.F. Rogerson
USSR	Department of Baltic Sea Academy of Sciences, Paldiski Street 2 200 105 Tallinn, Estonian SSR	38	A. Aitsam
Australia	Dept. of Services and Supply Chemistry Division, Adelaide SA	39	D.L. Harvey
	New South Wales State Fisheries Sidney, New South Wales	40	R. Chvojka
	Dept. of Fisheries and Wildlife Western Australia Marine Research Laboratory Waterman Western Australia	41	K. Francesconi

Table 6. Laboratories in Table 5 that have participated in previous ICES Exercises.

Country	Laboratory No.	Previous ICES Exercises			
		1st	2nd	3rd	4th
Belgium	1	x	x	x	x
Canada	2			x	x
France	9	x	x	x	x
Federal Republic of Germany	12	x	x	x	x
Ireland	18			x	
Netherlands	19	x	x	x	x
Norway	23			x	x
Norway	24	x	x		
United Kingdom	30	x	x	x	
United Kingdom	31	x	x	x	x
USA	36			x	x
USA	37			x	

Table 7. Results of the analysis of arsenic in Sample A (μg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
12	6	0.46	0.53	0.50	6
8	6	0.30	1.10	0.63	49
9	6	1.30	2.00	1.58	16
11	3	5.00	5.50	5.27	5
37	20			8.9	12
17	3	11.6	12.7	12.2	5
35	6	12.2	14.0	12.9	5
41	6	13.0	14.3	13.6	4
19	6	13.8	14.1	14.0	1
2	6	13.0	16.6	15.5	9
31	6	13.9	17.8	15.7	8
20	5	15.5	16.9	16.2	3
39	6	17	17	17	
21	6	18.1	19.4	18.8	3
23	6	18.0	21.4	20.2	6
4	6	16.0	27.0	20.7	18
AERE* Harwell England	6	13.6	15.8	15.0	6

*Analysis by neutron activation.

Table 8. Analysis of arsenic - summary of methods employed by analysts.

Laboratory No.	Mean value (μg/g)	Summary of method
12	0.50	WD/Reduction/FAA-heated quartz tube
8	0.63	WD/Reduction/Colorimetric using molybdate
9	1.58	WD/Reduction/FAA-heated quartz tube
11	5.27	WD/Reduction*/extraction/FAA-furnace
37	8.9	WD/FAA (no nickel salts present)
17	12.2	DA/Reduction/colorimetric using molybdate
35	12.9	DA/Reduction-AsH_3 collected in cold trap/FAA-heated graphite furnace
41	13.6	WD/Reduction/FAA-heated quartz tube
19	14.0	DA/Reduction/colorimetric using Ag diethyldithiocarbamate
2	15.5	WD/FAA in the presence of nickel salts
31	15.7	WD/Reduction**/AA-argon/hydrogen flame
20	16.2	X-ray fluorescence
39	17	WD/Reduction/AA-nitrogen/hydrogen flame
23	20.2	DA/Reduction/AA-argon/hydrogen flame
4	20.7	WD/FAA in the presence of nickel salts

Key:

WD - Wet digestion

DA - Dry ashing in the presence of MgO and $Mg(NO_3)_2$

Reduction - Reduce As to AsH_3 using $NaBH_4$

Reduction* - Reduction of As^{5+} to As^{3+} by ascorbic acid

Reduction** - Very strong concentration of $NaBH_4$ used to reduce As to AsH_3

FAA - Flameless atomic absorption

AA - Atomic absorption

Table 9. Results of the analysis of cadmium in Sample A (ng/g*).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
12	7	4	8	5	26
38	6	7	9	8	10
40	6	<10	<10	<10	
21	6	10	16	12	17
29	6	9	17	13	21
18	6	11	14	13	9
9	5	10	20	14	39
2	6	14	15	14	4
6	6	13	20	16	16
15	6	15	20	18	10
26(2)	6	16	24	19	15
30	4	20	20	20	
34	6	<10	< 20	< 20	
19	6	<4	38	< 20	66
26(1)	6	19	24	22	10
24	4	14	34	22	39
1	6	22	23	23	2
37	20			26	23
25	6	22	32	28	15
7	3	22	36	29	24
13	6	28	32	30	5
8	6	24	41	32	19
31	6	24	54	35	41
23	6	31	55	39	24
11	3	45	50	47	6
28	1			52	8
39	6	<70	< 70	< 70	
3	6	56	86	70	15
32	6	80	100	90	11
17	6	88	110	97	8
16	6	<20	220	100	70
4	6	<130	< 150	<140	6
33	6	200	400	280	28
14				320	
10	5	360	410	390	5
27	6	970	1 110	990	6

*1ng/g = 0.001 µg/g.

Table 10. Results of the analysis of chromium in Sample A (μg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
8	6	0.03	0.15	0.07	67
3	5	0.11	0.19	0.14	23
37	5			0.15	27
1	6	0.17	0.19	0.18	4
32	5	0.1	0.4	0.2	70
23	6	0.13	0.46	0.32	43
20	1			<0.4	
33	6	<0.4	<0.4	<0.4	
22	1			<1.0	

Table 11. Results of the analysis of copper in Sample A (µg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
20	1	<0.4	< 0.4	<0.4	
17	5	0.75	0.86	0.80	5
38	6	0.79	0.86	0.82	3
30	6	1.1	1.4	1.2	10
8	6	1.22	1.34	1.29	4
18	5	1.26	1.42	1.30	5
19	6	1.24	1.63	1.42	10
28				1.44	7
29	6	1.40	1.72	1.47	8
10	6	1.36	1.73	1.53	9
11	3	1.50	1.60	1.57	4
3	6	1.39	1.97	1.58	14
34	6	1.5	1.7	1.61	4
7	5	1.50	1.80	1.64	8
33	6	1.5	1.8	1.65	6
12	6	1.63	1.83	1.70	5
16	6	1.08	2.97	1.70	47
39	6	1.7	1.9	1.75	5
37	20			1.79	4
31	6	1.68	2.04	1.81	7
15	6	1.70	1.97	1.82	5
6	6	1.74	1.96	1.83	6
27	6	1.72	2.05	1.83	7
1	6	1.85	1.95	1.91	2
23	6	1.77	2.32	1.92	12
26(1)	6	1.7	2.4	1.9	13
25	6	1.6	2.5	2.0	20
26(2)	6	1.9	2.1	2.0	4
32	6	1.9	2.1	2.0	3
4	6	2.0	2.2	2.1	4
24	5	1.28	3.27	2.27	32
40	6	2.3	2.9	2.52	9
21	6	2.5	3.4	2.8	13
14				3.0	
9	4	3.4	4.2	3.8	12
41	6	2.1	6.4	4.0	45

Table 12. Results of the analysis of iron in Sample A (µg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
20	5	4.7	6.3	5.7	11
23	7	3.3	7.5	5.8	33
26(2)	6	5.9	6.7	6.2	4
24	5	6.7	8.5	7.5	9
26(1)	6	7.4	8.1	7.8	4
10	6	7.6	12.2	9.6	17
37	5			10.6	25
32	6	11.2	14.3	12.2	9
6	6	12.0	13.1	12.7	4
33	6	9.5	15.6	12.8	22
21	6	12	14	13	8
1	6	12.2	14.4	13.3	7
22	1			13.9	
27	5	15.0	15.9	15.5	3
8	6	13.3	18.3	15.6	12

Table 13. Results of the analysis of lead in Sample A (ng/g*).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
15	6	16	24	18	17
38	6	21	31	25	14
12	7	22	35	28	18
25	6	ND	420	<70	245
18	6	49	114	88	33
37	20			<100	
40		< 100	< 100	<100	
1	6	109	122	115	4
11	3	120	120	120	
21	6	110	150	130	11
6	6	148	163	154	3
30	6	140	200	162	14
29	6	112	213	163	22
13	6	152	201	172	11
9	3	170	190	177	6
26(2)	6	160	210	183	10
7	3	180	191	185	3
39	6	< 190	< 190	<190	
32	6	< 200	< 200	<200	
8	6	180	260	210	16
26(1)	6	190	270	225	15
31	8	200	260	225	10
16	6	100	540	230	70
3	5	150	360	240	32
34	6	< 100	< 300	<300	
2	6			297	4
24	5	270	540	352	32
28				420	24
23	6	140	600	447	40
4	6	350	< 570	<430	20
17	6	650	830	707	10
33	6	<1 000	1 700	2 800	
27	6	6 800	8 000	7 500	6

* 1 ng/g = 0.001 µg/g . ND = Not detected.

Table 14. Results of the analysis of manganese in Sample A (µg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
26(1)	6	0.52	0.56	0.54	3
26(2)	6	0.59	0.66	0.62	4
33	6	0.50	0.80	0.67	
23	4	0.53	0.82	0.67	19
1	6	0.72	0.75	0.73	1
22	1			0.8	
37	5			0.80	75
8	6	0.81	0.91	0.87	4
29	6	0.83	0.99	0.88	7
27	6			0.95	8
32	6	0.9	1.3	1.05	17
10	6	0.97	1.45	1.16	15
6	6	1.09	1.30	1.21	6
20	5	1.2	2.4	1.6	27
14				11.7	

Table 15. Results of the analysis of Mercury in Sample A (ng/g*).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
25	6	35	62	47	24
17	6	105	119	108	5
30	6	120	140	132	7
38	6	138	151	144	4
1	6	131	195	153	16
35	6	147	176	162	7
18	5	137	218	163	20
11	3	160	170	165	3
32	5	120	210	168	18
9	4	150	190	170	11
13	6	169	188	177	4
4	6	130	220	178	17
8	6	170	200	187	6
15	6	187	200	193	2
7	5	187	200	195	3
26(2)	6	169	223	201	10
24	6	200	210	203	3
6	6	194	222	204	5
5	5	200	215	206	3
31	6	190	230	207	8
22	1			211	
19	6	184	228	212	7
10	6	206	228	217	4
12	8	210	230	221	4
23	6	188	261	224	10
39	6	220	240	230	4
41	6	140	350	250	28
2	6	250	280	267	5
26(1)	6	246	316	276	10
21	6	260	340	307	10
40	6	300	410	330	12
3	4	40	720	340	80
16	6	290	460	370	19

*1ng/g = 0.001 µg/g.

Table 16. Results of the analysis of mercury in Sample B (ng/g*).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
8	1			<10	
2	5	16	19	19	7
30	6	16	20	19	8
35	6	19	32	24	21
38	2	26	31	28	12
29	6	27	31	29	5
12	9	25	37	30	14
31	6	30	40	32	13
7	5	28	37	32	12
19	6	33	37	35	6
6	6	34	36	35	3
27	6			40	25
39	6	40	40	40	
17	6	42	48	46	5
10	6	38	60	47	19
33	6	40	60	50	22
22	1			52	
36	6	46	61	54	11
18	5	48	86	58	29
25	6	47	69	59	15
24	6	52	70	59	13
41	6	20	100	60	50
11	3	55	65	62	9
4	6	< 10	< 90	<63	46
21	6	60	70	67	8
26(2)	6	62	82	69	11
26(1)	6	78	97	85	9
15	6	92	95	93	1
40	6	90	110	95	8
23	4	81	156	99	38
3	6	50	200	127	51
5	5	113	145	131	9
1	6	179	261	211	18
16	6	200	330	250	24

*1ng/g = 0.001 µg/g.

Table 17. Results of the analysis of selenium in Sample A (µg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
9	4	0.9	1.0	0.95	6
4	6	1.2	1.9	1.5	18
20	5	1.4	1.7	1.5	9
41	6	1.52	1.87	1.70	8
39	6	1.7	1.8	1.72	2
2	6	1.48	2.00	1.82	10
23	6	1.98	2.34	2.21	7
22	1			<25	

Table 18. Results of the analysis of zinc in Sample A (µg/g).

Laboratory No.	No. of replicates	Minimum value	Maximum value	Mean value	Coefficient of variation
28				12.8	6
29	6	14.1	22.4	16.8	21
25	7	17.4	18.2	17.8	2
26(2)	6	16.5	19.7	18.0	7
26(1)	6	17.1	20.3	18.3	7
10	6	17.2	21.0	18.8	7
18	6	19.5	20.0	19.7	1
20	5	19.5	21.1	20.2	4
12	7	19.3	21.1	20.3	3
15	6	19.8	21.2	20.4	3
1	6	20.2	21.4	20.6	2
30	6	20.0	22.0	20.7	4
34	6	19.6	21.4	20.7	3
36	6	20.0	22.0	20.7	4
39	6	21	21	21	
11	3	21.0	21.5	21.3	1
37	20			21.6	3
24	4	20.9	22.2	21.7	3
19	6	19.4	25.6	22.1	10
27	6	21.4	23.9	22.6	4
23	6	22.3	24.6	23.3	3
7	5	22.0	25.4	23.3	6
22				23.5	
17	6	21.1	24.9	23.6	6
6	6	21.7	25.0	23.7	5
40	6	20.0	29.0	23.8	12
32	6	23.6	24.5	24.0	2
31	6	23.4	24.9	24.1	2
4	6	23	27	24.5	6
8	6	24.8	25.4	25.1	1
16	6	22.1	28.2	25.6	9
21	6	25.0	29.0	27.3	6
41	6	24.5	33.8	27.6	12
9	4	25.7	30.2	28.5	7
33	6	30.9	39.0	33.2	9
3	6	35.1	39.5	37.3	5

Table 19

LIST OF LABORATORIES PARTICIPATING IN THE 3rd ORGANOCHLORINE EXERCISE

Number		Number	
1	Dr W Vyncke Rijksstation voor Zeevisserij 8400 Oostende Ankerstraat 1 BELGIUM	8	Professor Jaakko Paasivirta Department of Chemistry University of Jyväskylä Kyllikinkatu 1-3 SF-40100 Jyväskylä 10 FINLAND
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5	Dr K Orbaek Ministry of Environment National Food Institute Mørkhøj Bygade 19 DK-2860 Søborg DENMARK		FEDERAL REPUBLIC OF GERMANY
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Table 20. Organochlorine Residues in Commercial Fish Oils (Concentrations in μg/g)

Information	α HCH	ɣ-HCH	Dieldrin	pp'DDE	pp'TDE	op DDT	pp'DDT	HCB	PCB(1254)
Crude trawler[a]	0.003	0.006	0.16	0.22	0.22	0.04	0.36	0.097	1.97
Refined trawler[a]	0.003	0.007	0.17	0.28	0.25	0.06	0.34	0.080	1.92
Crude Icelandic[b]	0.002	0.003	0.14	0.57	0.17	0.08	0.24	0.116	2.62
Refined Icelandic[b]	0.002	0.004	0.18	0.58	0.15	0.03	0.12	0.101	3.15
Crude Capelin	0.001	0.011	0.049	0.090	0.005	0.021	0.110	0.058	0.38
Crude Capelin	0.012	0.007	0.03	0.06	0.04	0.03	0.06	0.034	0.56
Refined Capelin	0.010	0.009	0.06	0.07	0.05	0.02	0.08	0.037	0.60
Crude Mackerel	0.008	0.011	0.05	0.14	0.09	0.03	0.05	0.047	1.86
Refined Mackerel	0.004	0.014	0.06	0.10	0.09	0.04	0.14	0.034	1.45

[a] Mixed fish oils

[b] Cod liver oils

Table 21. Analyses of ICES Organochlorine Intercalibration Sample No. 4 (Results in µg/kg)

Laboratory No.	HCB	α-HCH	β-HCH	γ-HCH	Heptachlor epoxide	Dieldrin	pp'-DDE	pp'-TDE	pp'-DDT	op-DDT	PCB	Other Residues
1	-	-	-	-	-	-	-	-	-	-	1190	
2	101	91	<10	-	-	92	32	96	109	<10	191	
3	84	75	<40	<10	-	75	(164)	(231)	(203)	(216)	1700	(DDT group possibly over-estimated)
5	84	57	<7	<4	51?	64	76	110	100	60?	380	?identity doubtful
7 Method A	-	-	-	-	-	-	80	80	80	-	900	
Method B	-	-	-	-	-	-	80	70	80	-	1020	
8	43	-	-	<2	-	12	33	114	220	-	1160	
9	-	12	-	<4	-	-	56	69	120	-	644	
10	-	-	-	136	-	-	16	-	30	-	750	
11	50	40	-	-	-	-	70	160	170	-	1200	
13	116	72	-	-	-	-	-	-	-	-	8000	
15	-	-	-	-	-	-	103	-	-	-	509	
16 Method 1	54	32	-	-	-	32	54	83	195	-	411	
Method 2	40	33	-	6	-	59	-	76	-	-	261	
20	42	40	<10	8	-	65	62	60	72	<10	260	
21	64	49	<10	6	-	-	100	75	100	<20	1130	
22	86	55	-	25	-	129	116	87	131	128	Present	op-TDE 74
23	-	-	-	-	-	-	-	-	-	-	270	
25	70	60	<10	20	10	100	60	50	40	40	530	
26	83	73	<10	3	<10	100	123	123	33	45	500	
27 Sample 1	63	48	<10	16	<10	80	80	54	71	<10	277	
Sample 2	69	59	<10	13	<10	64	52	36	47	<10	270	
28	41	50	80	<10	22	109	139	<20	305	<100	1630	TCNB 4, QCB12, Endosulfan 6
29	58	53	-	24	16	119	61	62	-	-	583	op-TDE 174, QCB11, Endrin 22

/Cont'd.

Table 21 (ctd)

Laboratory No.	HCB	α-HCH	β-HCH	ɣ-HCH	Heptachlor epoxide	Dieldrin	pp'-DDE	pp'-TDE	pp'-DDT	op-DDT	PCB	Other residues
31	-	-	-	-	-	-	100	79	110	75	1300	
32	52	131	-	13		-	116	189*	171	-	467	
34	80	60	< 2	6	-	90	110	< 50	170	70	400	QCB6
35	-	-	-	-	-	-	74	52	158	-	190	
37	34	60	25	21	-	82	88	110	134	51	720	α-chlordane 50, β-chlordane 50
40	100	10	1	1	-	-	210	70	120	-	1500	Chlordane 240
												Toxaphene 1000 - 5000
41	-	48	-	-	-	-	-	-	-	-	-	
42	58	1	< 5	13	< 5	49	90	< 5	110	21	380	
44	70	50	-	10	20	90	340	180	90	-	700	Endrin 90, Toxaphene 2500
												Heptachlor 20, Oxychlordane 20
												Transchlordane 40, cis-chlordane 150
												Transnonachlor 70

* With op-DDT QCB = pentachlorobenzene TCNB = tetrachloronitrobenzene

Table 22. Results Obtained by Analysts using Capillary Columns (µg/kg).

Laboratory No.	HCB	α-HCH	ɣ-HCH	Dieldrin	DDE	TDE	DDT	PCB	PCB Ref.	PCB Quant.
10	-	-	136*	-[a]	16*	-	30	750	DP5	Several peaks
25	-	-	-	-	60	50	40	-		
27[d]	63 69 (66)[e]	48 59 (54)	16 13 (15)	80 64 (72)	80 52 (66)	54 36 (45)	71 47 (59)	277 270 (274)	1254	2 peaks
31	-	-	-	-[a]	100	79	110	1300*	1254	2 peaks
32	52	131*	13	-[a]	116	189*[b]	171	467	A.50	24 peaks
34	80	60	6	90[c]	110	< 50*	170	400	A.60	10 peaks
Mean	66.00	57.00	11.33	81.00	90.40	58.00	96.67	472.75		
s.d.	14.00	4.24	4.73	12.72	25.74	18.36	63.49	201.41		
No. of Analyses	3	2	3	2	5	3	6	4		
* No. Omitted	0	1	1	0	1	2	0	1		

[a] H_2SO_4 treatment [b] With op-DDT [c] Separate analysis for dieldrin [d] Two samples [e] Means of two values

Table 23. Results Obtained by Analysts using Sulphuric Acid Pretreatment (µg/kg)

Laboratory No.	HCB	α-HCH	γ-HCH	Dieldrin	DDE	TDE	DDT	PCB	PCB Ref.	PCB Quant.
1	-	-	-	-	-	-	-	1190	1254	Perchlorination
7B	-	-	-	-	80	70	80	1020	A.50/A.60	7 peaks
8	43	-	<2*	12[a]	33	114	220	1160	1254	5 peaks
9	-	12	<4*	-	56	69	120	644	DP.5	5 peaks
10	-	-	136*	-	16*	-	30*	750	DP.5	Several peaks[c]
11	50	40	-	-	70	160	170	1200	DP.5	?
21	64	49	6	-	100	75	100	1130	1254	4 peaks
23	-	-	-	-	-	-	-	270	1254	3 peaks
31	-	-	-	-	100	79	110	1300	1254	2 peaks[c]
32	52	131*	13	-	116	189[b]*	171	467	A.50	24 peaks [c]
34	80	60	6	90[a]	110	<50*	170	400	A.60	10 peaks [c]
35	-	-	-	-	75	52	158	190	1254	Several peaks
40	100	10	1	-	210*	70	120	1500	A.50	Several peaks
Mean	64.83	34.20	6.50	-	75.60	86.13	131.72	863.15		
s.d.	21.58	22.34	4.93	-	33.01	34.61	52.66	431.84		
No. of Analyses	6	5	4	-	10	8	11	13		
* No. Omitted	0	1	3	-	1	2	0	0		

[a] Separate analysis [b] With op-DDT [c] Capillary column

Table 24 Results Obtained using Clean-up (without H_2SO_4), Pre-GLC Separation and Packed GLC columns (µg/kg)

Laboratory No.	HCB	∝-HCH	ɣ-HCH	Dieldrin	DDE	TDE	DDT	PCB	PCB Ref.	PCB Quant.
2	101	91	-	92	32	96	109	191	1254	3 peaks
3	84	75	<10*	75	-	-	-	1700*	1254/1260	5 peaks
5	84	57	< 4	64	76	110	100	380	1254	Several peaks
7A	-	-	-	-	80	80	80	900	A.50+A.60(1:1)	7 peaks
15	-	-	-	-	103	-	-	509	A.60	3 peaks
20	42	40	8	65	62	60	72	260	1254	4 peaks
25	70	60	20	100	-	-	-	530	1254	1 peak
26	83	73	3	100	123	123	33	500	1254	DCB
28	41	50	<10*	109	139	<20*	305*	1630*	1254	3 peaks
29	58	53	24	119	61	62	-	583	A.50	Several peaks
37	34	60	21	82	88	110	134	720	1260	?
42	58	1*	13	49	90	< 5*	110	380	1254	5 peaks
44	70	50	10	90	340*	180	90	700	1254	?
Mean	65.91	60.90	14.14	85.91	85.40	102.63	91.00	513.91		
s.d.	21.32	14.93	7.73	21.20	31.16	38.79	30.38	208.81		
No. of Analyses	11	10	7	11	10	8	8	11		
* No. Omitted	0	1	3	0	1	2	1	2		

Table 25 Mean Values and Coefficients of Variation of Data Obtained by Different Analytical Techniques (µg/kg)

Residue	Capillary GLC	Sulphuric Acid Clean-up	Adsorbent Clean-up, pre-GLC Separation
HCB	66.00 (21.2)*	64.83 (33.3)	65.91 (32.3)
α-HCH	57.00 (7.4)	34.20 (65.3)	60.90 (24.5)
γ-HCH	11.33 (41.7)	6.50 (75.8)	14.14 (54.7)
Dieldrin	81.00 (15.7)	-	85.91 (24.7)
DDE	90.40 (28.5)	75.60 (43.7)	85.40 (36.5)
TDE	58.00 (31.7)	86.13 (40.2)	102.63 (37.8)
DDT	96.67 (65.7)	131.72 (40.0)	91.00 (33.4)
PCB	472.75 (42.6)	863.15 (50.0)	513.91 (40.6)

* % coefficient of variation in parentheses

Table 26 Results Obtained by Analysts using Packed GLC Columns without Pre-GLC Residue Separation (µg/kg)

Laboratory No.	HCB	α-HCH	γ-HCH	Dieldrin	DDE	TDE	DDT	PCB
1	-	-	-	-	-	-	-	1190
7B	-	-	-	-	80	70	80	1020
8	43	-	< 2	12	33	114	220	1160
11	50	40	-	-	70	160	170	1200
13	116	72	-	-	-	-	-	8000*
21	64	49	6	-	100	75	100	1130
22	86	55	25	129	116	87	131	-
35	-	-	-	-	74	52	158	190*
Mean	71.80	54.00			78.83	93.00	143.17	1140.00
s.d.	29.67	13.49			28.40	38.73	50.68	72.46
No. of analyses	5	4			6	6	6	5
* No. omitted	0	0			0	0	0	2

Table 27 Pooled Values of Analytical Results

Residue	No. of Values	No. Omitted	Mean (µg/kg)	s.d.	c.v. %
HCB	22	0	67.09	21.93	32.7
α-HCH	22	1	48.86	21.27	43.5
γ-HCH	14	6[c]	11.36	8.08	71.1
Dieldrin	17	0	78.76	29.49	37.4
pp'-DDE	24	3	79.50	30.19	38.0
pp'-TDE	21	5[d]	88.14	33.89	38.4
pp'-DDT	23	2	113.13	49.88	44.1
PCB[a]	15	1	451.40	204.36	45.3
PCB[b]	13	0	863.15	431.84	50.0

[a] excluding values from sulphuric acid pre-treatment

[b] from sulphuric acid pre-treatment only

[c] 5 values below limit of detection

[d] 3 values below limit of detection

Table 28. Residue Concentrations (µg/kg) and Coefficient of Variation* from Analyses of Oils in 1972, 1975 and 1979

Residue	2A (1972) Unspiked Fish Oil	2B (1972) Spike in Fish Oil	3B (1975) Spike in Corn Oil	4 (1979) Unspiked Fish Oil
HCB	-	-	46 (40.6)	67 (32.7)
α-HCH	-	-	41 (15.5)	49 (43.5)
γ-HCH	80 (70)	750 (13.5)	52 (27.9)	11 (71.1)
Dieldrin	115 (55)	1440 (6.8)	93 (24.3)	79 (37.4)
pp-DDE	450 (30)	5260 (19.7)	101 (13.5)	80 (38.0)
pp-TDE	290 (29)	3040 (17.8)	103 (10.2)	88 (38.4)
pp-DDT	430 (21)	4990 (10.6)	93 (6.5)	113 (44.1)
PCB	1890 (48)	9960 (10.6)	96 (9.0)	451[a] (45.3) 863[b] (50.0)

* % coefficient of variation in parentheses

[a] Without sulphuric acid treatment

[b] With sulphuric acid treatment

APPENDIX I

INSTRUCTIONS FOR THE ANALYSIS OF THE TWO ICES REFERENCE SAMPLES:

SAMPLE	INFORMATION REQUIRED
A	Cu, Zn, Pb, Cd, Hg (total) and As. (optional metals - Se, Cr, V, Co, Mn, Ni, Ag and Fe)
B	Hg

1) The sample should be analysed by the methods currently in use in your laboratory.

2) All analyses should be done 6 times.

3) Your methods should be calibrated using working standards prepared in accordance with the attached instructions.

4) The results of your analyses should be expressed on a dry weight basis. Dry weight determinations should be carried out on a separate sample of the fish flour.

5) On completion of this exercise, the following information should be returned to the coordinator.

   a) Full results of all metal analyses made on the samples.
   b) Full details of the analytical procedure, including blanks and detection limits (plus a description of the method of calculation of this parameter).
   c) The make and model number of the instrumentation used in these procedures.
   d) Xerox copies of all calibration curves and wherever possible xerox copies of the recorder data.

PREPARATION AND STORAGE OF WORKING STANDARDS

Mercury

1. Stock standards (1 000 µg/g) should be made up in 1N H_2SO_4 or 1N HCl and stored in glass bottles.

   Fresh stock solutions should be prepared every 6 months or when the level of the current stock solution in the glass bottle falls below the half-way mark.

2. Working standards. This should be prepared daily by dilution of the above stock solution, using 1N acid together with sufficient 6% $KMnO_4$ solution to produce a distinct pink colour in the final solution.

   Please check the mercury content of your $KMnO_4$ solution as this can contain very high levels of mercury (a solution of Potassium Dichromate may be used as an alternative to Potassium Permanganate).

   In practice, these working standards should be prepared immediately before use and should be discarded one they have achieved a bench life of ca. 2 hours.

Other Metals

1. Stock standards (1 000 µg/g) should be made up in 1N acid and can be stored in either glass or plastic bottles. (Alternatively, these standards may be purchased from any of the large chemical manufacturers or suppliers.) Fresh stock standards should be made (or purchased) every 6 months or when the level of the current stock standard solution in the bottle falls below the half-way mark.

2. Working standards. These should be prepared daily by dilution of the above stock standard using 1N acid.

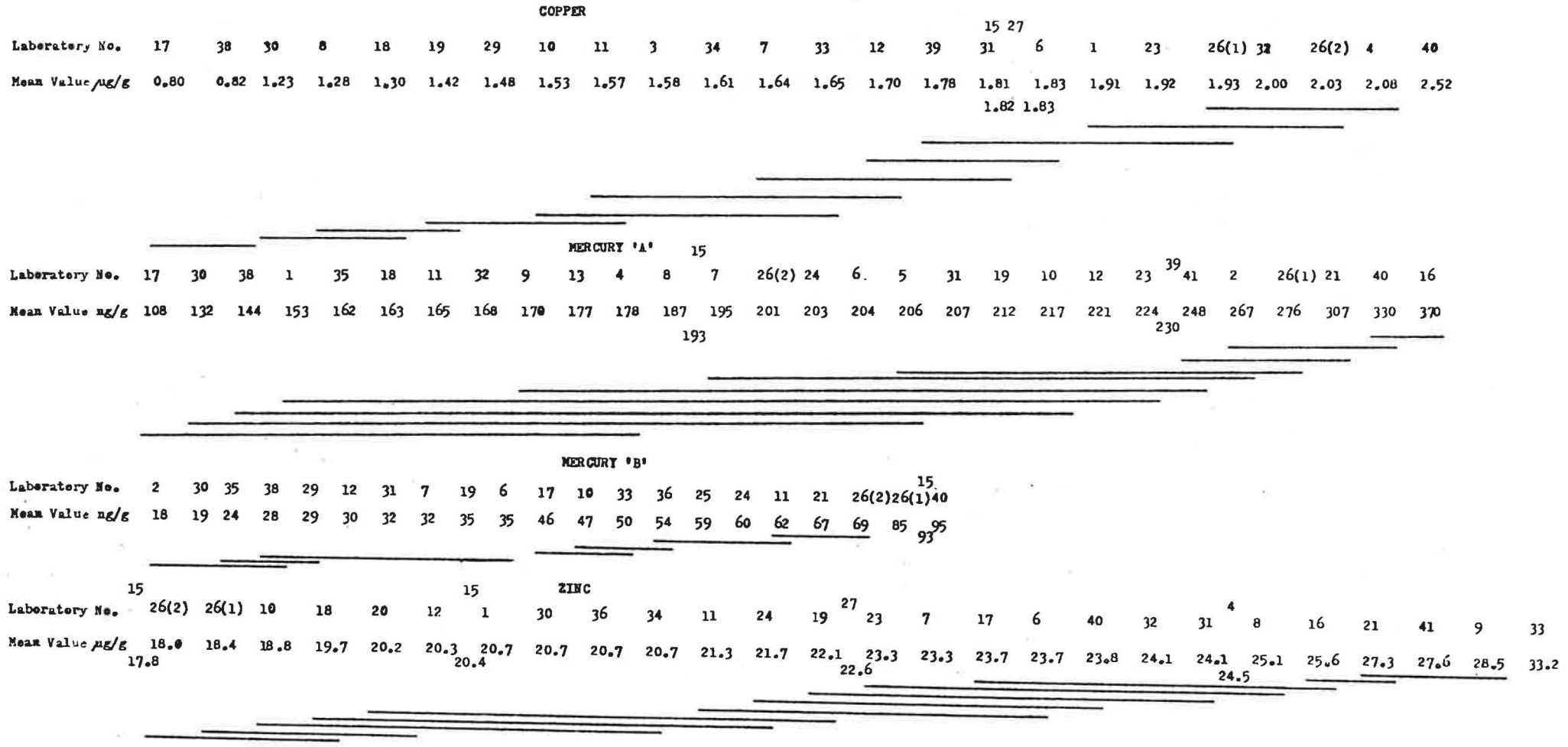
APPENDIX II

MULTIPLE RANGE TEST

The common practice for testing the homogeneity of a set of n treatment means is to use an analysis of variance. The procedure alone, however, falls short of satisfying all the practical requirements. When the analysis of variance rejects the homogeneity hypothesis, it gives no decisions as to which of the differences among the means may be considered significant and which may not. The multiple range test pinpoints these significant differences. The data necessary to perform the test are the treatment means and the standard error of each mean. It is convenient to display the means in ranked order and to test differences in a set pattern, the largest mean minus the smallest, the largest minus the second smallest, up to the largest minus the second largest; then the second largest minus the smallest, the second largest minus the second smallest, and so on. A set of "shortest significance ranges" are calculated from tables of special "significant studentized ranges" and each difference between two means is significant if it exceeds the corresponding shortest significant range; otherwise, it is not significant.

This procedure and several alternatives are described by R. O'Neill and G.B. Wetherill in a paper entitled "The Present State of Multiple Comparison Methods", Journal of the Royal Statistical Society, Series B, Volume 33, No.2, 1971, pp.218-250.

Figure 1 RESULTS OF THE MULTIPLE RANGE TESTS - COPPER, MERCURY 'A' AND 'B', ZINC DATA



APPENDIX III

SUMMARY OF THE ANALYTICAL PROCEDURE AND INSTRUMENTATION USED BY PARTICIPANTS IN THE 4TH ICES TRACE METAL INTERCOMPARISON EXERCISE

Laboratory No.	Procedure	Instrumentation
1	Lead and Cadmium - 1.5g was dry ashed at 450°C. Residue dissolved in 2.5 ml HNO_3 (+ 1ml H_2O_2). Diluted to 50 ml. 10 µl used for injection.	Perkin Elmer 303 + HGA*
2	Lead - 0.5g digested with 10 ml conc HNO_3 at 80°C-90°C. Final volume = 20 ml (50% HNO_3). Standard addition technique (10 µl sample + 10 µl sample + 10 µl standard).	Perkin Elmer - 370A and HGA 2100. Deuterium background.
	Cadmium - 0.5g digested with 5 ml conc HNO_3 at 80°C-90°C. Final volume = 10 ml. Standard addition technique (10 µl sample + 10 µl standard).	Perkin Elmer - 403 HGA 74 and HGA 2100
3	Lead and Cadmium - 1g digested with 10 ml conc HNO_3 at 100°C. Reduced volume to 1 ml, final volume = 10 ml (0.8N HNO_3). 5 µl used for injection.	Techtron - AA5, carbon rod model 63. Background correction BC-6.
4	Lead and Cadmium - 1-3g digested with conc HNO_3 and H_2SO_4 at 140°C. H_2O_2 added to eliminated HNO_3. Diluted to 100 ml. Standard addition technique 15 µl used for injection.	IL 152 - graphite furnace. Deuterium background correction.
5(a)	Lead and Cadmium - 1g digested with 15 ml conc HNO_3 and 3 ml $HClO_4$. HNO_3 distilled off and final volume made up to 50 ml. Standard addition technique - 50 µl injected.	Perkin Elmer 420 and HGA 76. Deuterium background.
5(b)	As above but aqueous sample was extracted with dithizone/toluene. Re-extracted from organic phase using 0.5N HCl. 50 µl of this solution was then injected.	"
6	Lead and Cadmium - 1g dry ashed at 450°C. Residue dissolved in 20 ml HNO_3, diluted to 25 ml.	Perkin Elmer HGA 76.
7	Lead - 0.2g was digested with 5 ml HNO_3 (70%). Volume reduced to 0.5 ml and diluted to 10 ml. Standard addition technique - (2 µl sample + 6 µl standard).	Varian Techtron No. 1100 and CRA 63. Background correction - BC6.
	Cadmium - as above but final solution made up in 0.1 N H_2SO_4.	"

*) HGA - Heated Graphite Atomiser.

Laboratory No.	Procedure	Instrumentation
8	Lead and Cadmium - 0.15g was digested with 2 ml HNO_3 and 2 ml $HClO_4$ at 110°C, diluted to 10 ml. 2 ml aliquot evaporated to dryness, taken up in 0.4 ml HNO_3 (5%). Standard addition technique.	Perkin Elmer 403 and HGA - 76. Deuterium background.
9	Lead and Cadmium - 2.0g digested with 20 ml conc HNO_3 - evaporated to 5 ml and then diluted to 25 ml. Standard addition technique (20 µl sample).	Perkin Elmer 603 and HGA - 76. Deuterium background.
10	Lead and Cadmium - 0.1gm was digested with 0.75 ml (24:24:1:HNO_3, $HClO_4$, H_2SO_4) at 300°C. The sample was buffered with 5 ml of 1M Sodium Acetate/-0.2M Sodium Chloride. Plated at 1000mV for 30 mins, stripped at 60mV/sec.	ASV[1] - Environmental Sciences Associated Model 2014.
11	Lead and Cadmium - 1g was digested with 5 ml conc HNO_3 at 130°C-140°C. Evaporated to dryness. Final volume made up to 25 ml (HNO_3 - 5%).	Perkin Elmer - 305 and HGA - 2100.
12	Lead and Cadmium - 1.6g was digested with 10 ml HNO_3 at 50°C. Final volume 25 ml.	IL 151 (flame) + deuterium background.

1) ASV - Anodic Stripping Voltametry.

APPENDIX IV

ICES ORGANOCHLORINE INTERCALIBRATION PROGRAMME

ICES Sample No.4 - Crude Fish Oil

This oil is suitable for the analysis of a number of organochlorine compounds and should be examined for the following residues, together with any others which can be identified.

Residue	Suggested Detection Limit
α - HCH δ - HCH HCB	0.002 mg/kg
β - HCH pp - DDE pp - DDD pp - DDT op - DDT Dieldrin	0.01 mg/kg
PCBs	0.05 mg/kg (quote reference standard formulation)

It is recommended that an initial tenfold dilution should be used in a pure solvent. Report all results in terms of weight of oil (not volume), giving details of the analytical technique.

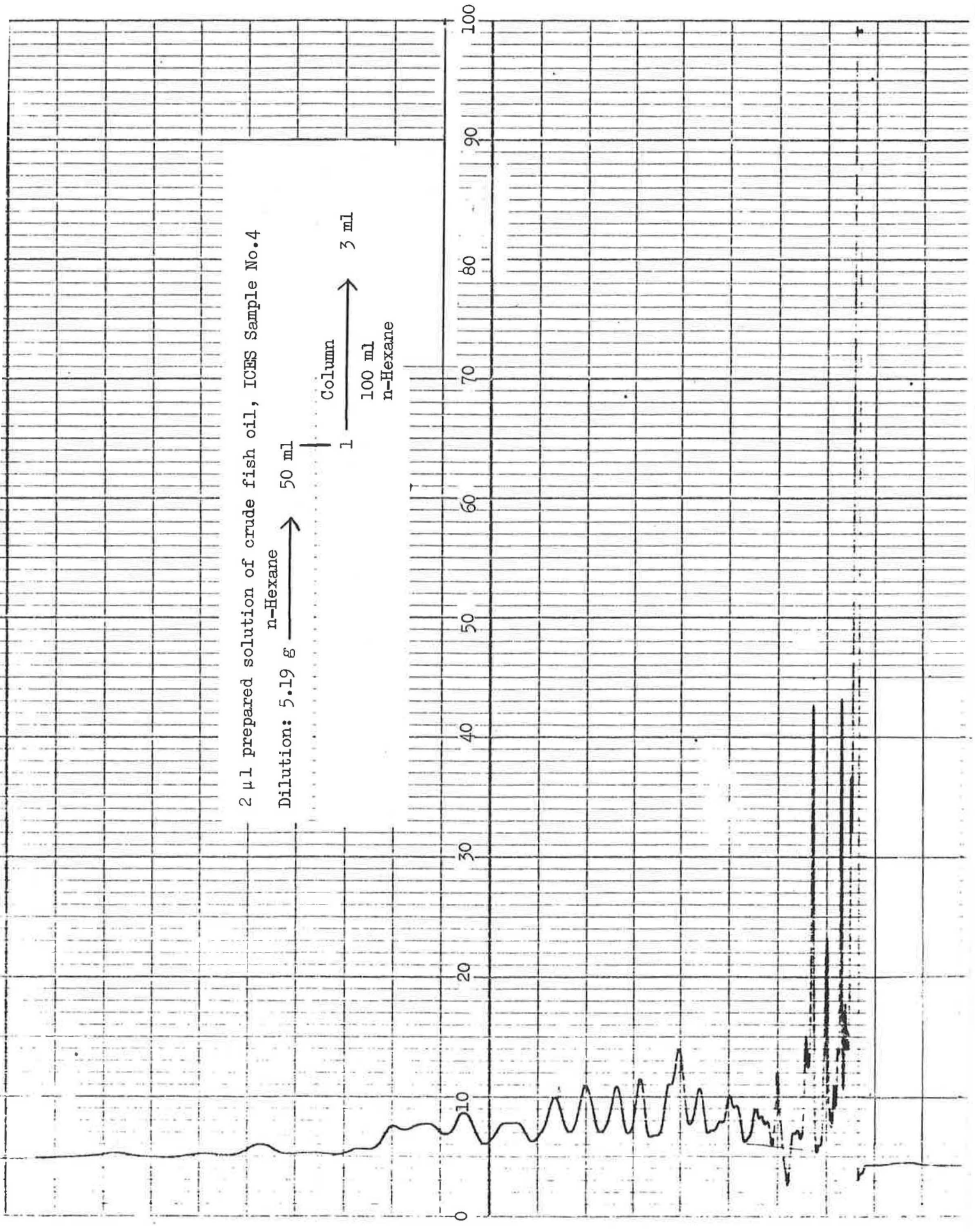
Specimen chromatograms of the fish oil and analytical standards are requested. A chromatogram of the solvent used (usually hexane) after 100-fold concentration should also be provided.

Please send you results to Mr A.V. Holden,
Freshwater Fisheries Laboratory,
Faskally,
Pitlochry PH16 5LB,
SCOTLAND.

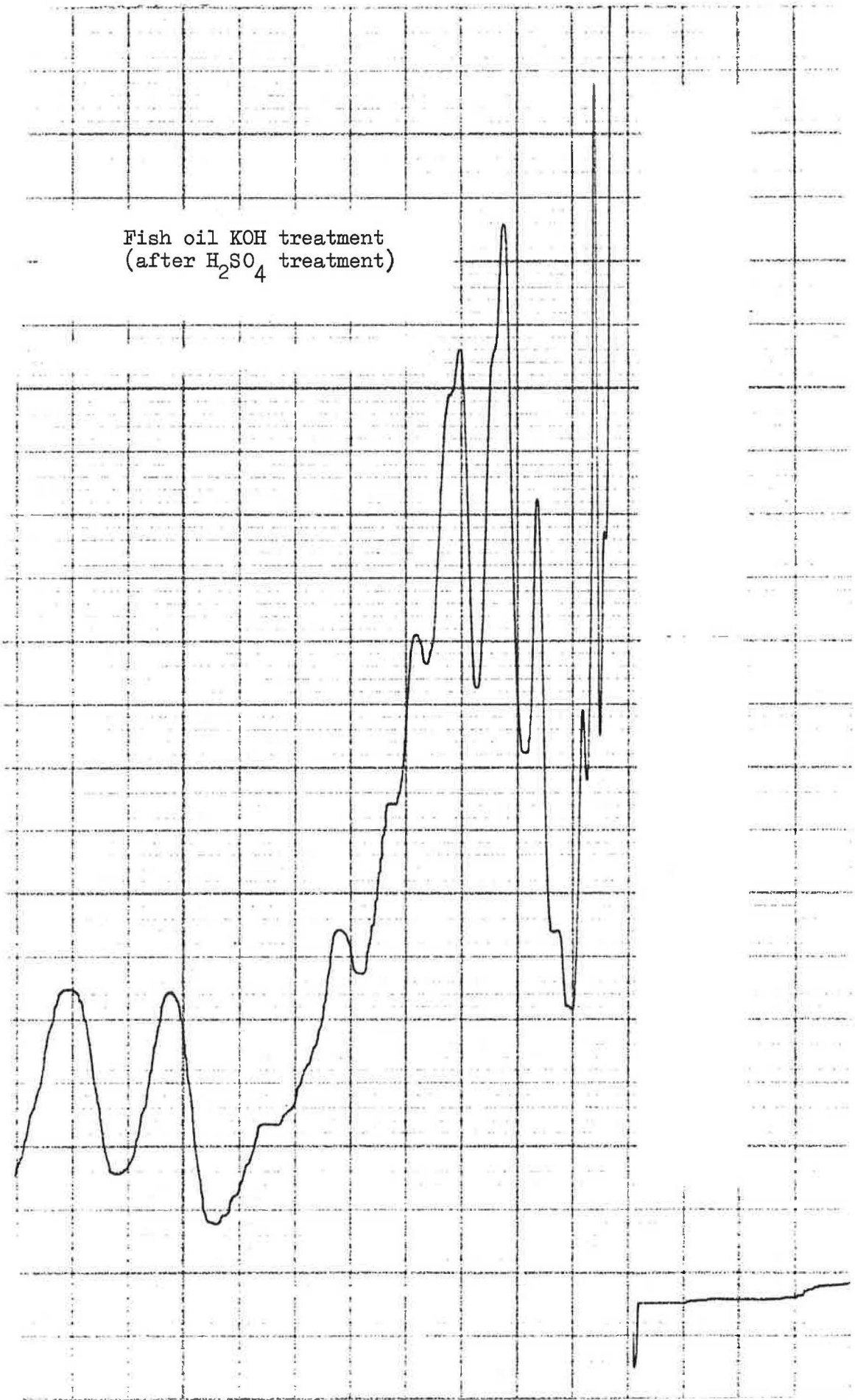
APPENDIX V

EXAMPLES OF CHROMATOGRAMS PRODUCED FROM ICES SAMPLE NO.4

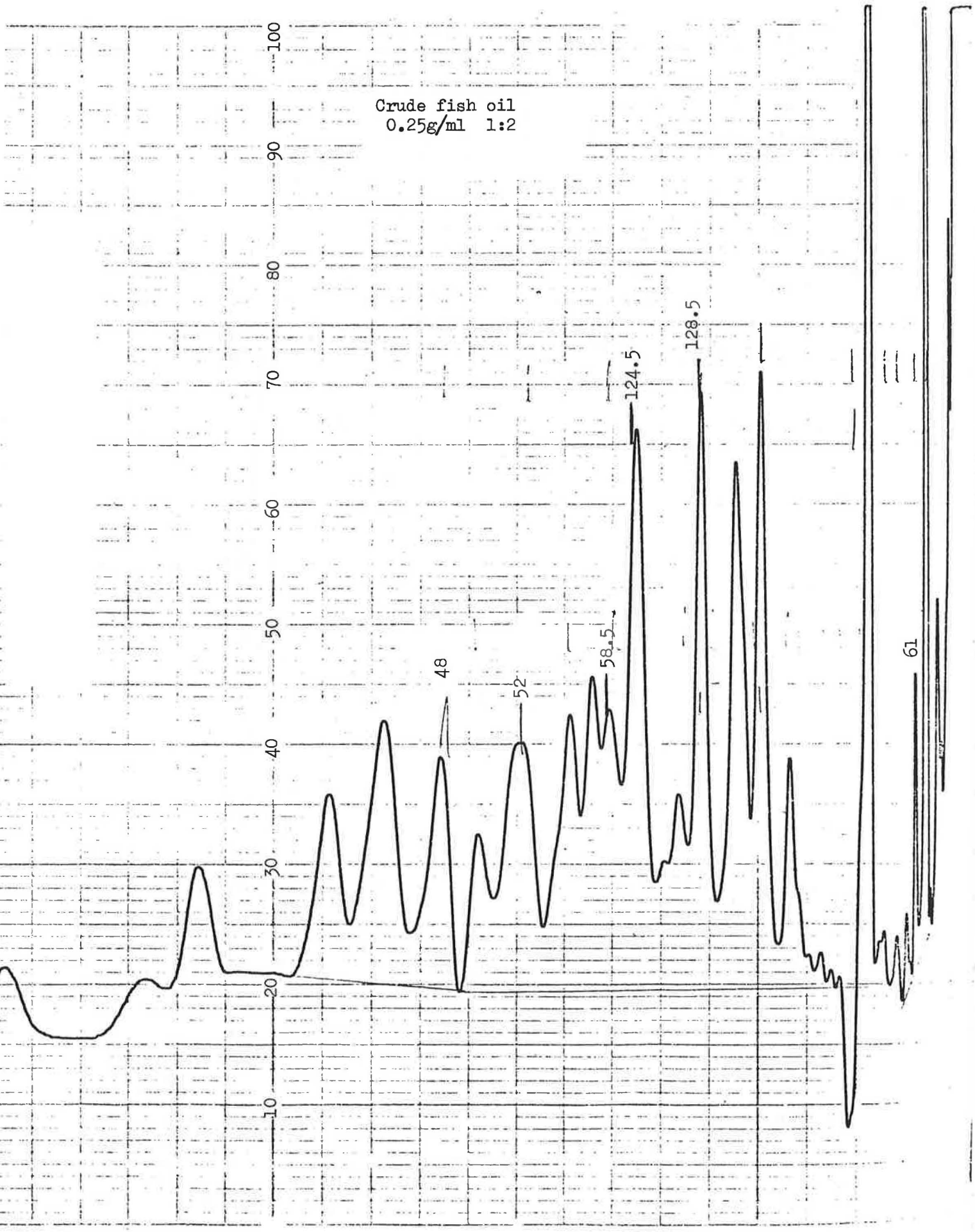
Appendix V, Figure A. Adsorbent clean-up. No pre-GLC separation.



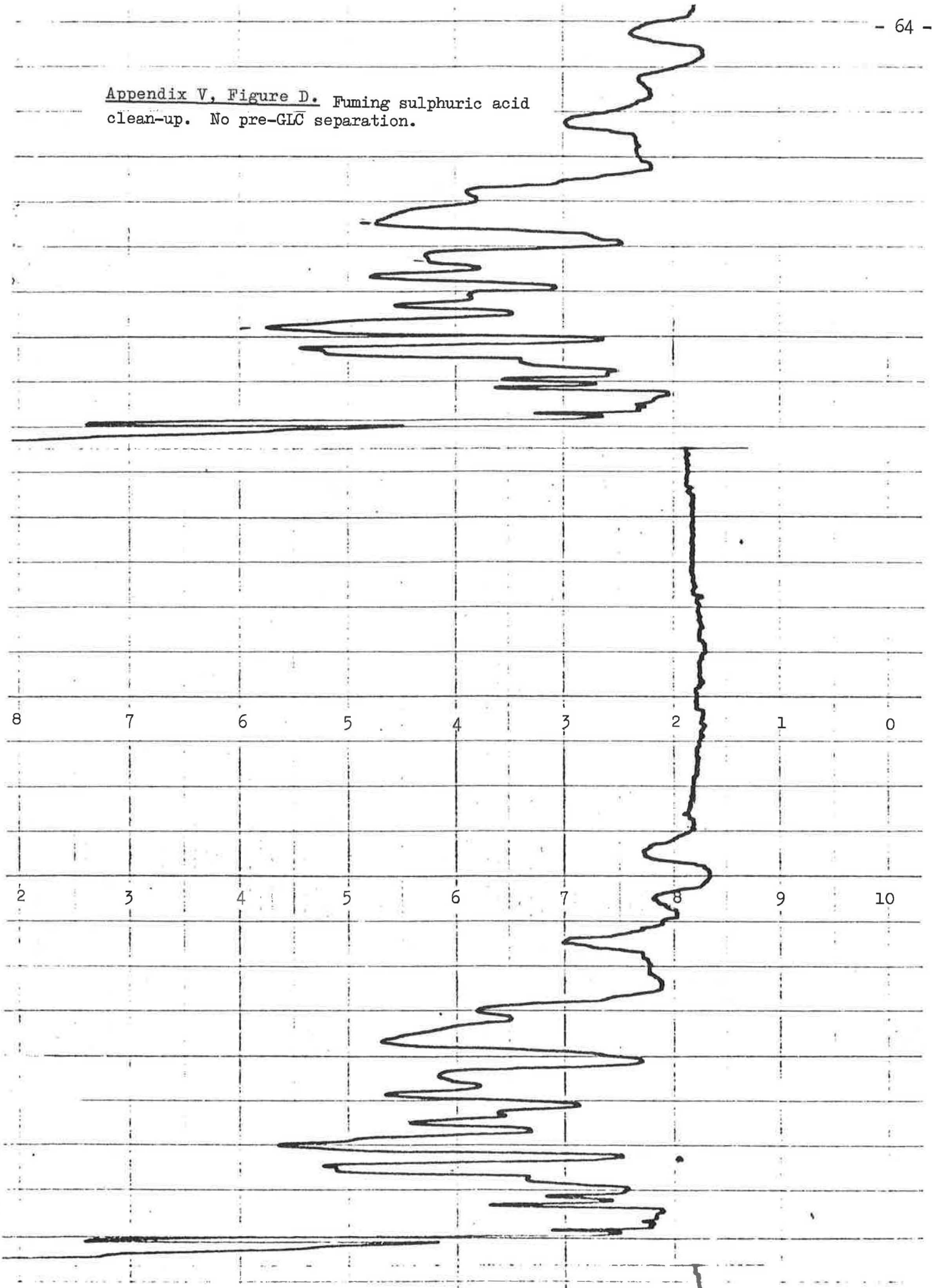
Appendix V, Figure B. Sulphuric acid clean-up, KOH treatment. No pre-GLC separation.



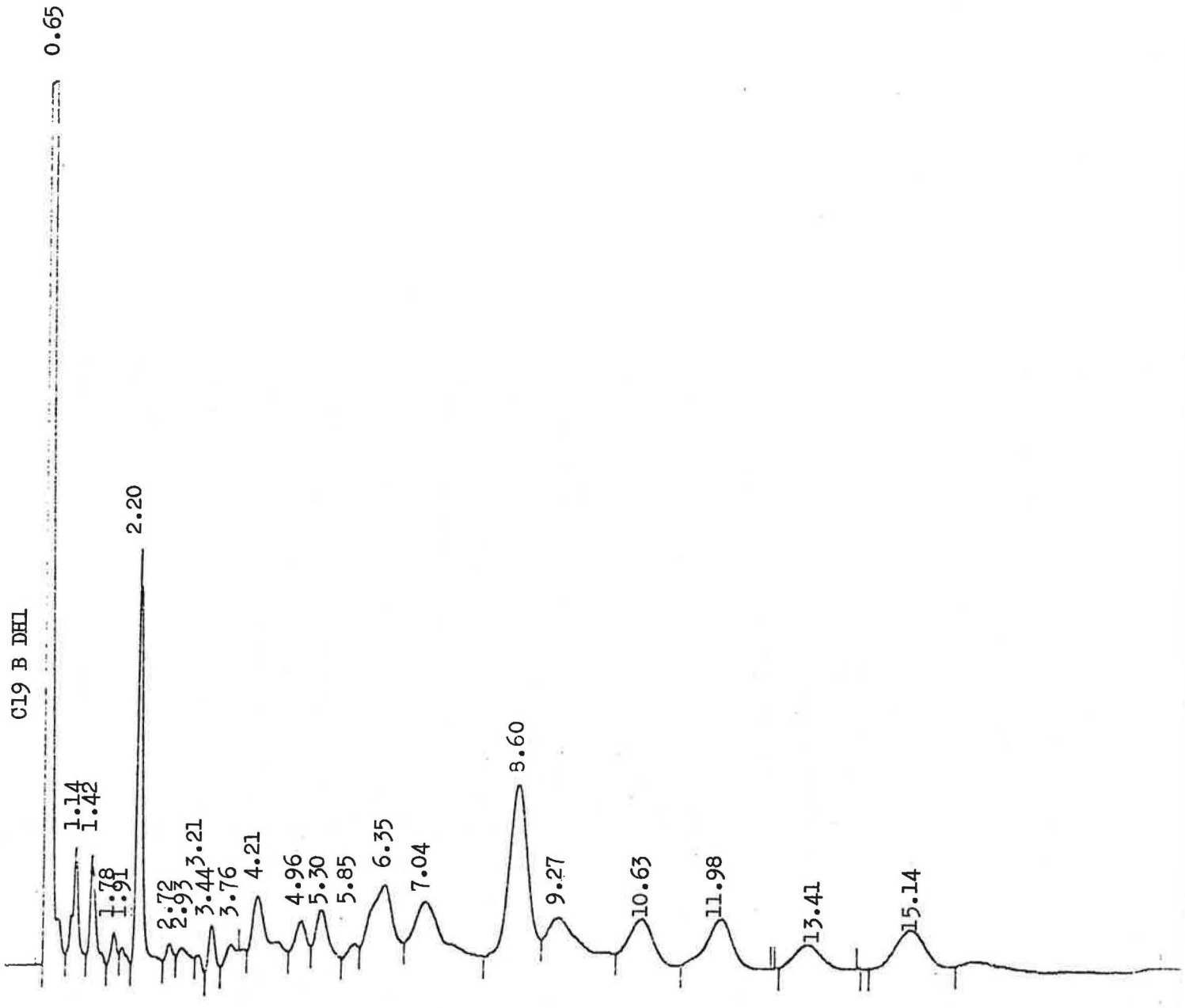
Appendix V, Figure C. Florisil clean-up. No pre-GLC separation.



Appendix V, Figure D. Fuming sulphuric acid clean-up. No pre-GLC separation.



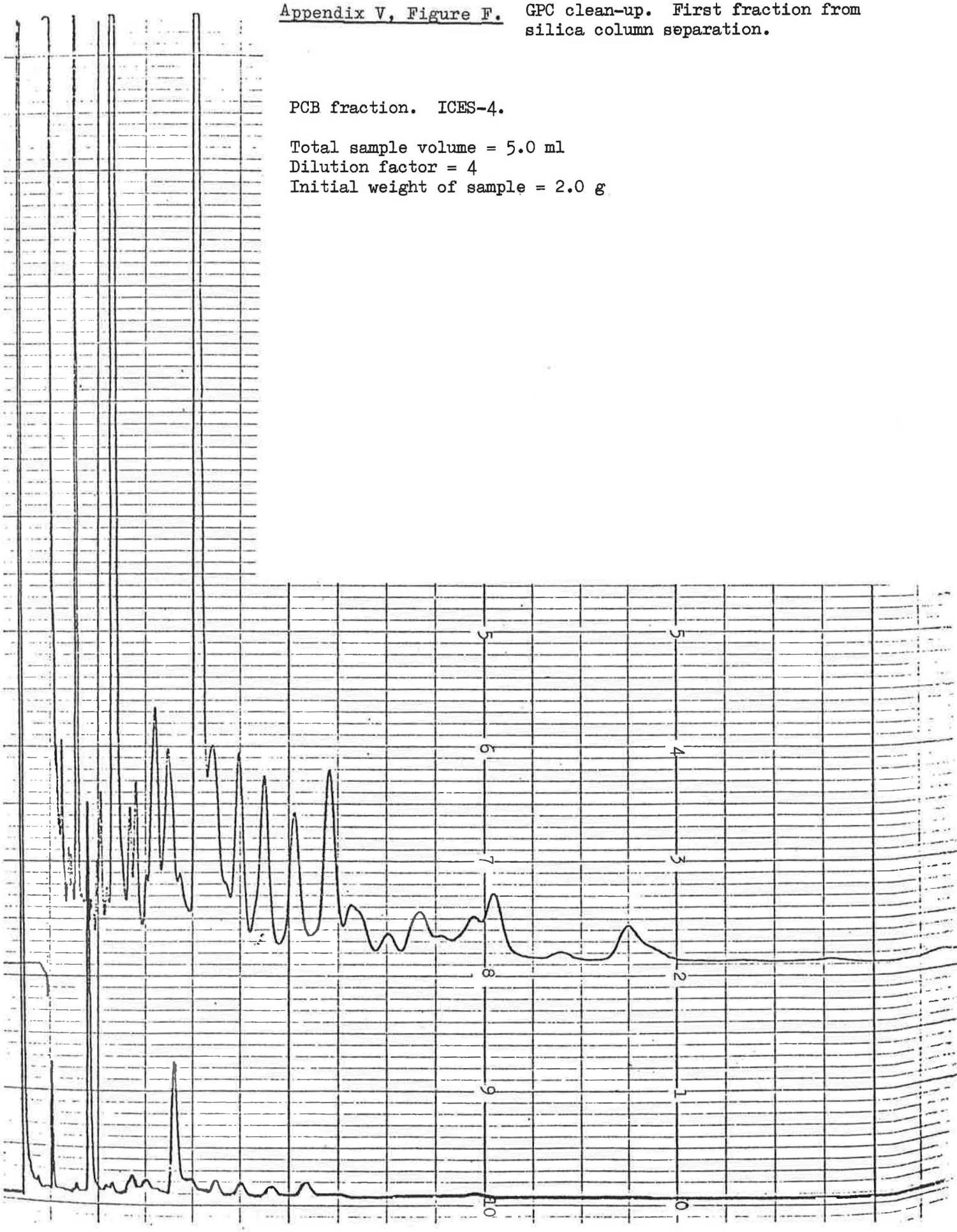
Appendix V, Figure E. Alumina clean-up. First (PCB) fraction from silica column separation.



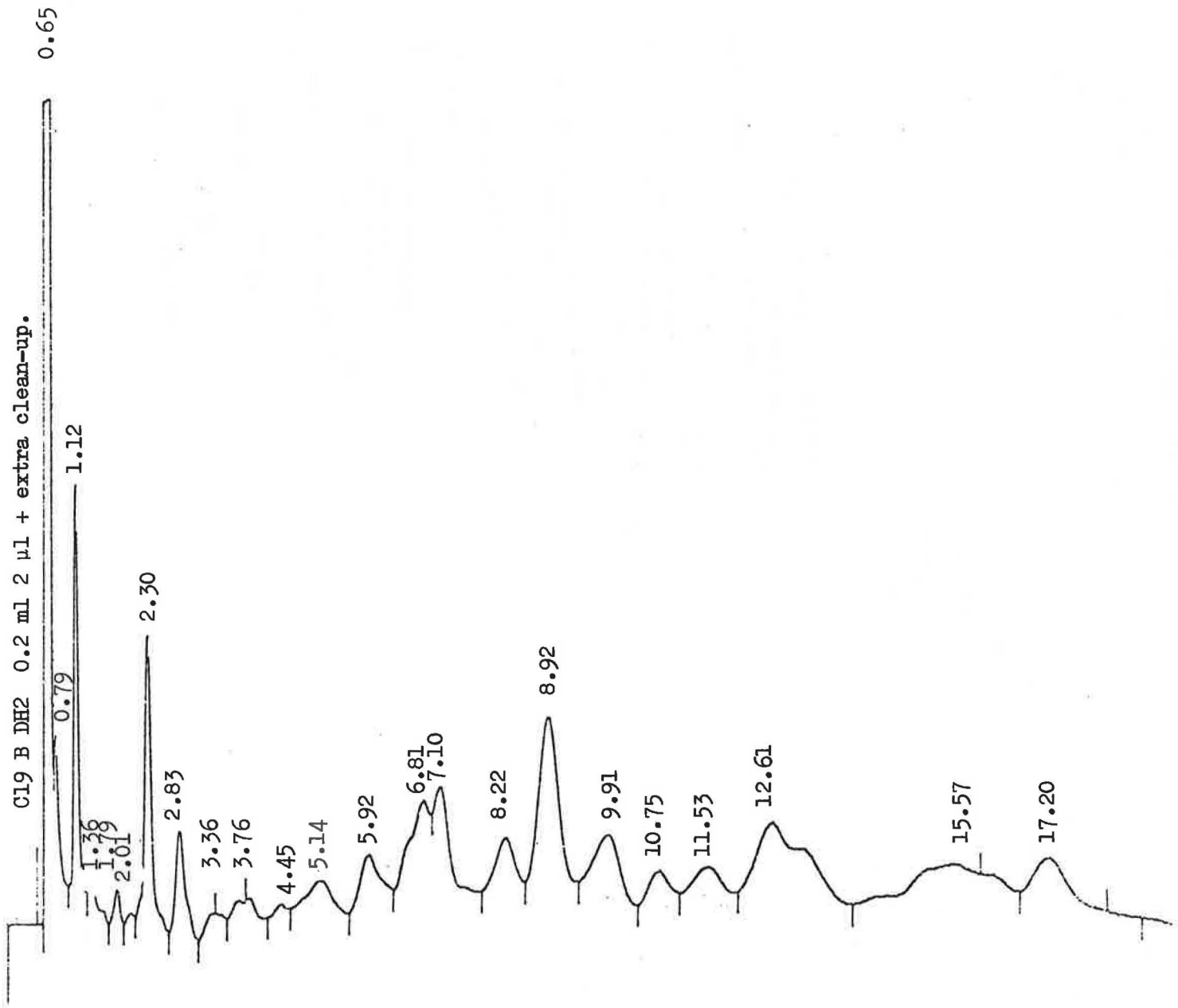
Appendix V, Figure F. GPC clean-up. First fraction from silica column separation.

PCB fraction. ICES-4.

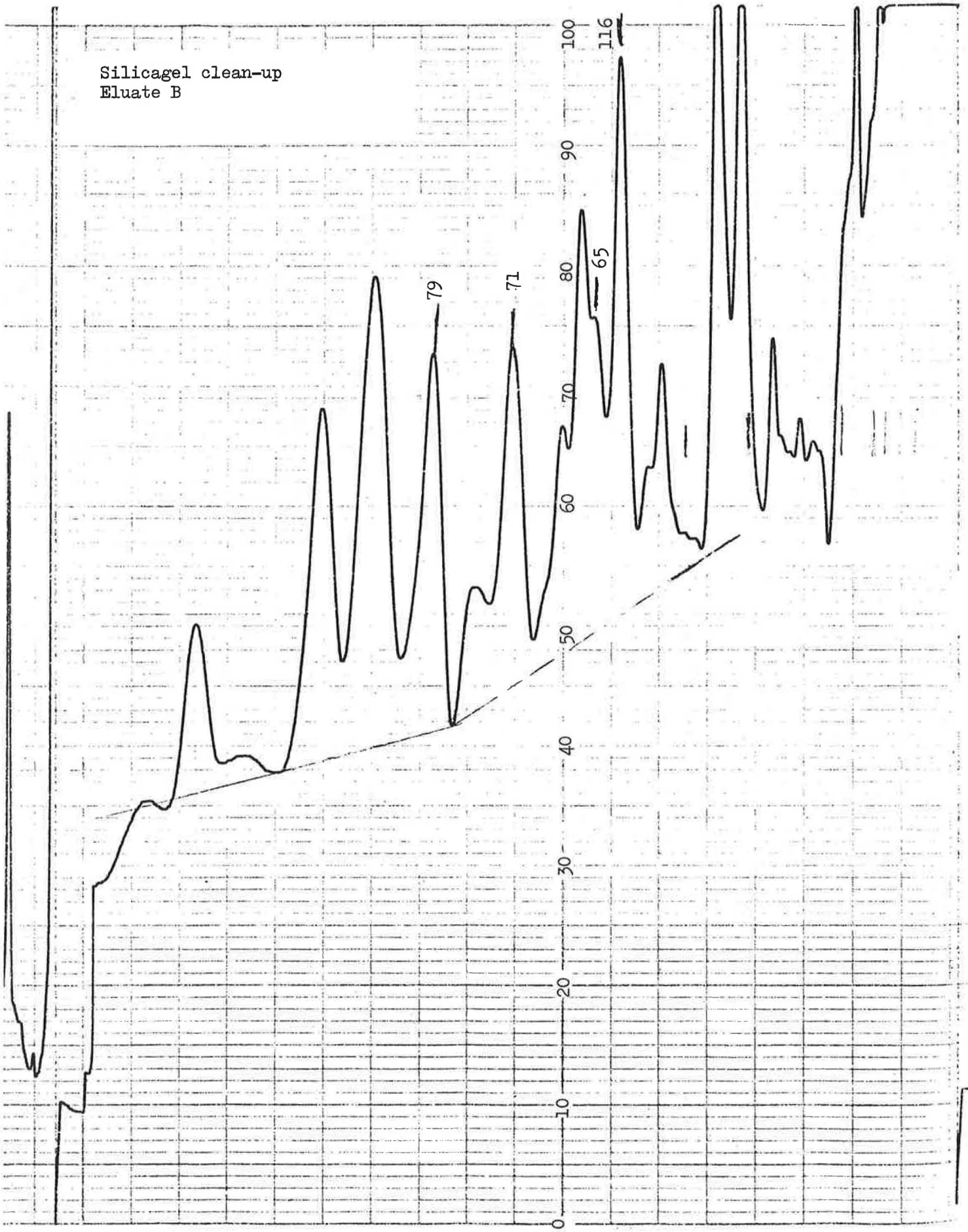
Total sample volume = 5.0 ml
Dilution factor = 4
Initial weight of sample = 2.0 g



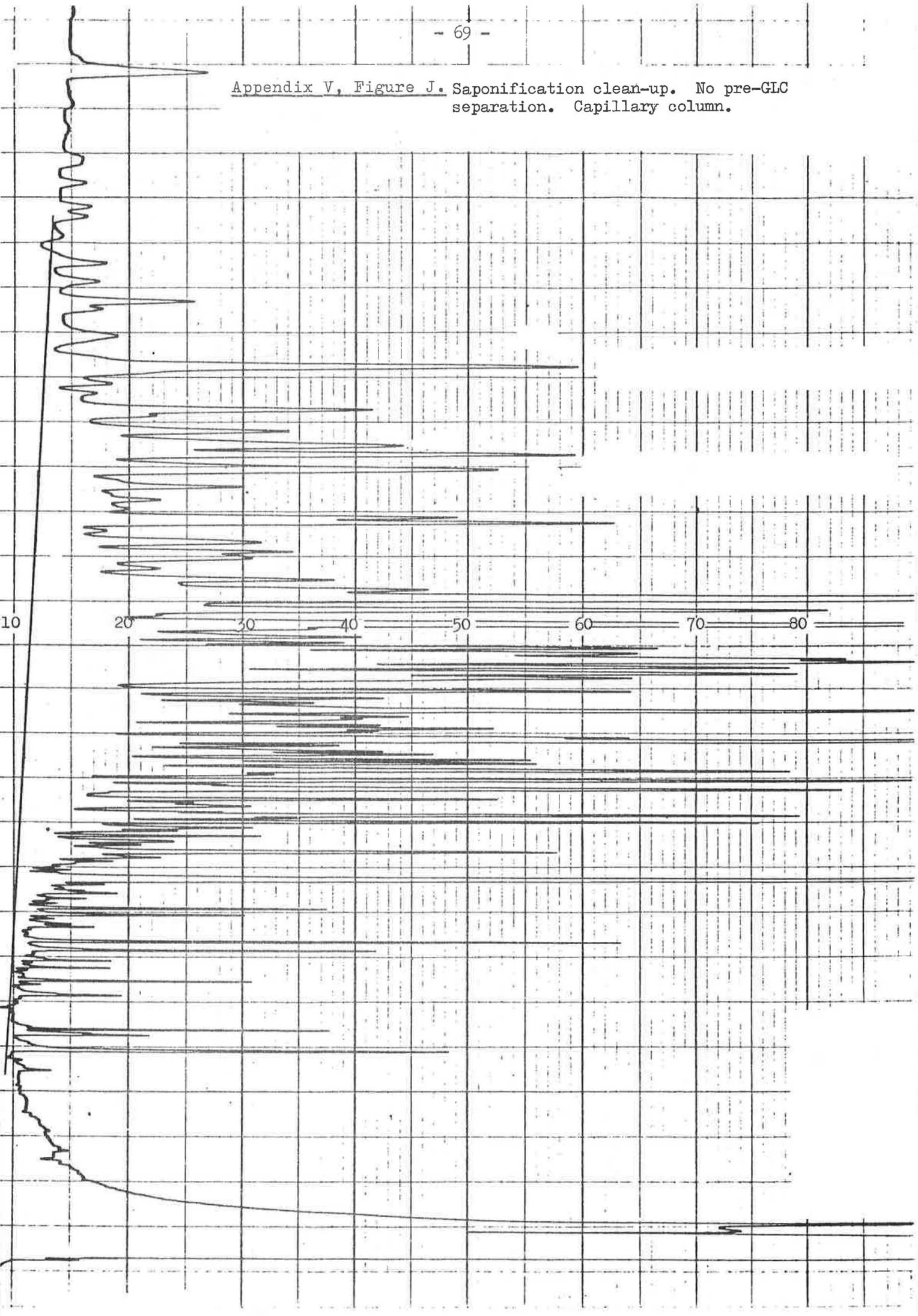
Appendix V, Figure G. Alumina clean-up. Second (pesticide) fraction from silica column separation.



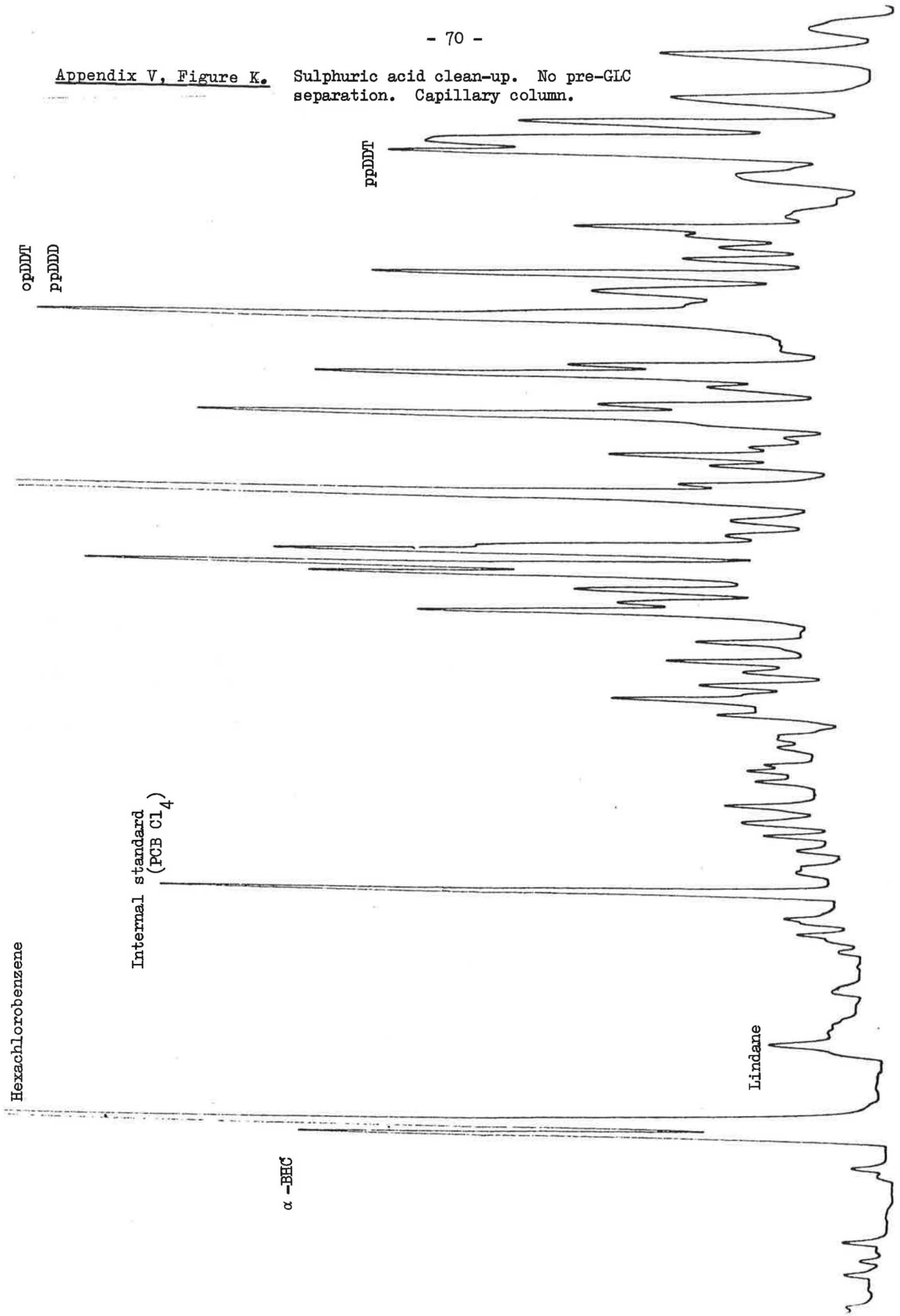
Appendix V, Figure H. Florisil clean-up. Second fraction from silica column separation.



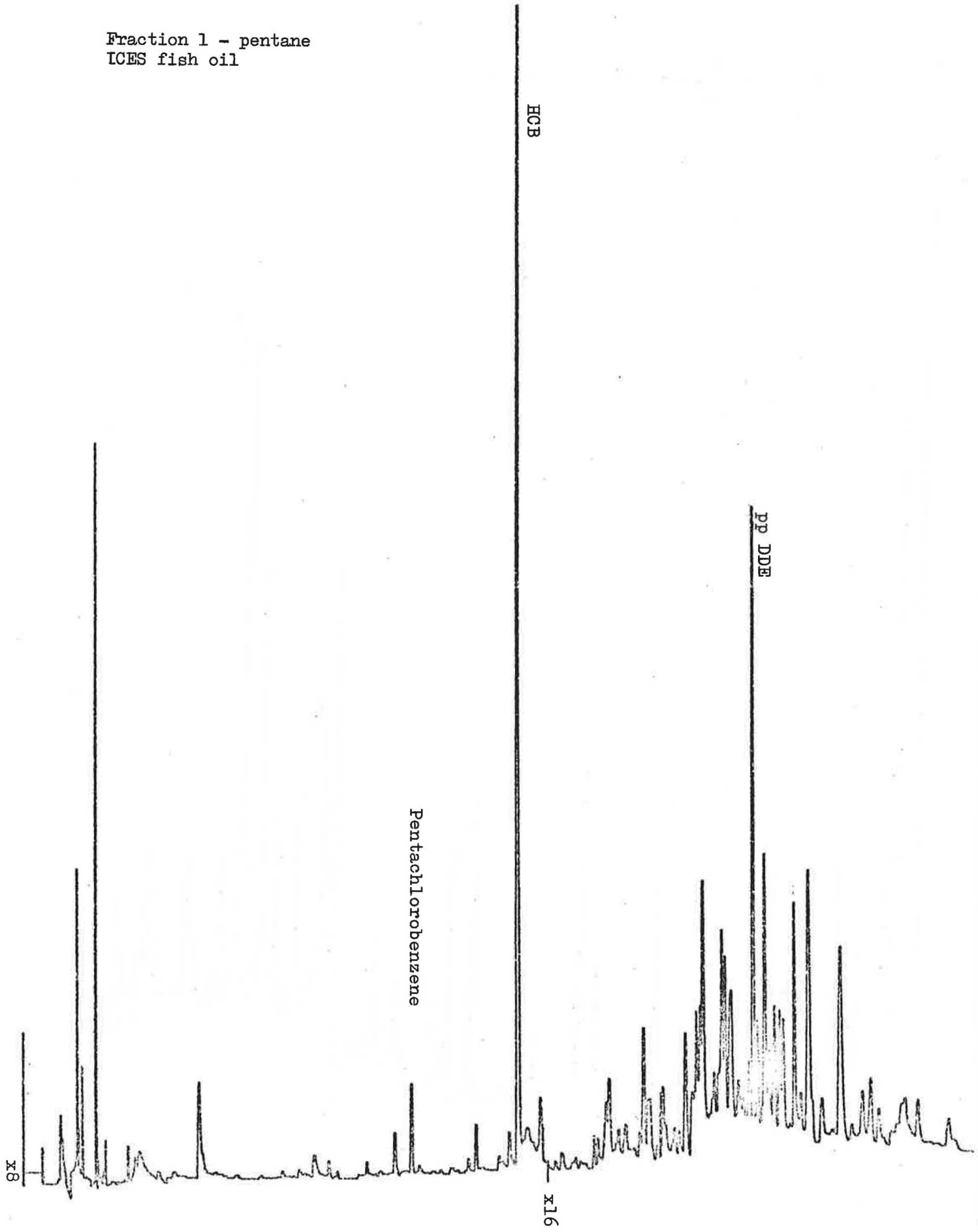
Appendix V, Figure J. Saponification clean-up. No pre-GLC separation. Capillary column.



Appendix V, Figure K. Sulphuric acid clean-up. No pre-GLC separation. Capillary column.

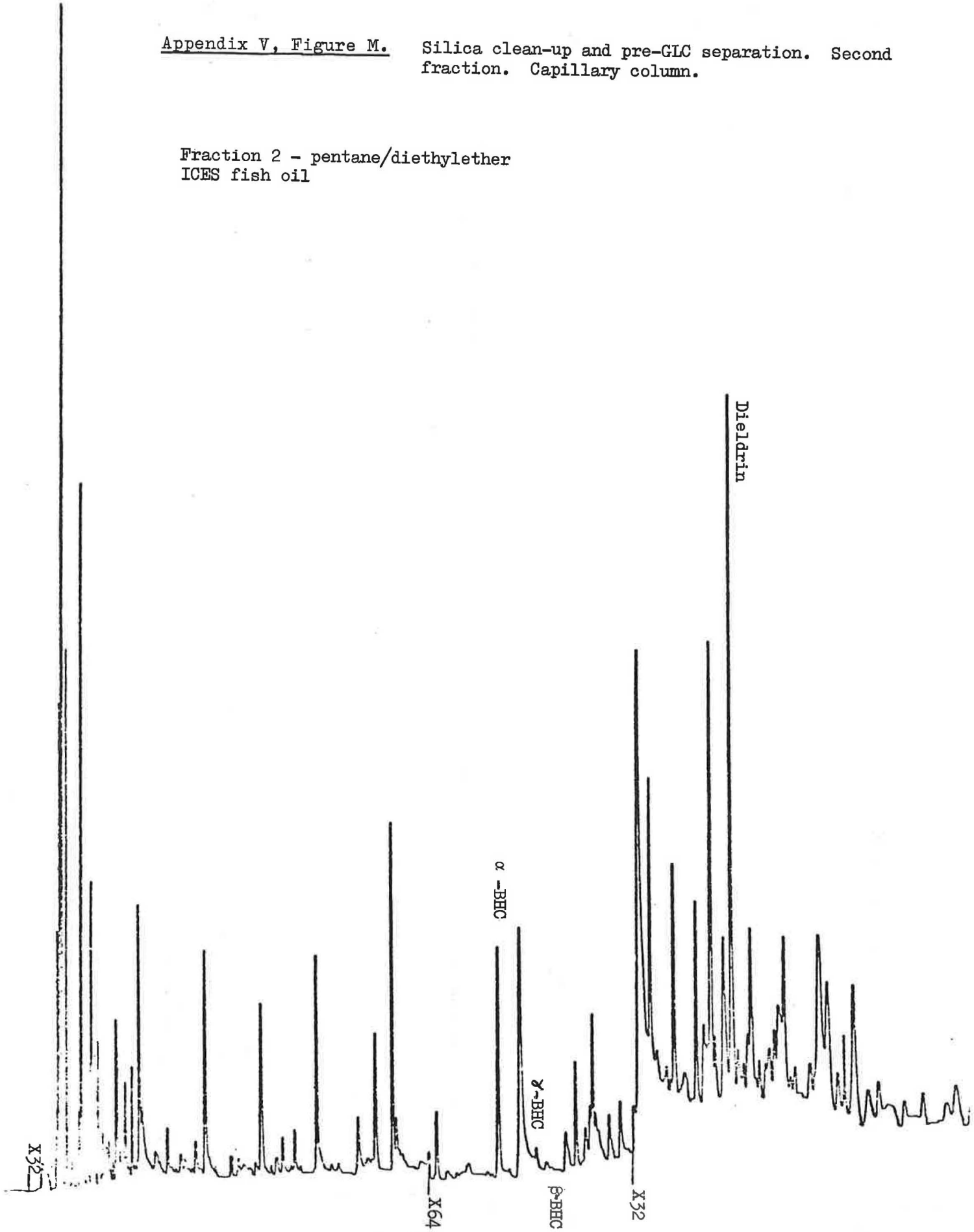


Appendix V, Figure L. Silica clean-up and pre-GLC separation. First fraction. Capillary column.



Appendix V, Figure M. Silica clean-up and pre-GLC separation. Second fraction. Capillary column.

Fraction 2 - pentane/diethylether
ICES fish oil



APPENDIX VI

Details of Analytical Procedures used by Participants in the Organochlorine Intercalibration

Laboratory No.	Extraction Solvent	Clean-up Method	Pre-GLC Separation	GLC Column (length x bore, capillary underlined)	Column Packing	Column Temperature °C (* programmed)	Confirmation Method
1	Acetone/hexane hexane-ether	H_2SO_4	None	2m x 3mm (o.d.)	3% SE-30 on Chromosorb Q AW-DMCS	200	PCB by perchlorination
2	Hexane	Florisil (Al_2O_3 for PCB)	Florisil TLC on Al_2O_3	(1) 1.85m x 4mm (for HCB/PCB)	3% SP-2100 on Supelcoport	200	Chemical reactions
				(2) 0.15m x 2mm (out) + 1.70m x 2mm (in) (for pesticides)	3% SP-2100/3% OV-210 on Supelcoport	200	
					1% SP-2100/2% SP-2401 on Supelcoport		
3	Hexane	Florisil	Florisil	(1) 1.8m x 3mm (o.d.)	4% SE-30/6% SP-2401 on Supelcoport	215	None
				(2) 1.8m x 6mm (o.d.)	2% XE-60 on Chromosorb W	185	None
5	Pet. ether	Florisil	Silica	1.8m x 2mm	(1) 0.8% DC-200 3.2% QF-1 on Chromosorb W (2) 3% DEGS (3) OV-17	170	3 GLC (2) for pesticides (3) for PCB, DDE
7A	Dichloromethane	TLC on SiO_2	TLC	1.8m x 2mm	2 pts 8% QF-1 + 1 pt 4% SF-96 on Chromosorb W AW-DCMS	175-200 *	
7B	Hexane	H_2SO_4	None	1.8m x 2mm	2 pts 8% QF-1 + 1 pt 4% SF-96 on Chromosorb W AW-DCMS	175-200 *	CrO_3, KOH
8	Hexane	H_2SO_4, KOH (TLC for dieldrin)	None	1.5m x 1.5mm	35 pts 4% SF-96 + 65 pts 8% QF-1 on Chromosorb W	190	KOH
9	Hexane	H_2SO_4	Silica	1.9m x 4mm	3% OV-1 on Chromport XXX	190	None
10	Hexane	H_2SO_4	None	28m x 0.25mm (WCOT)	SE-30	180-220 *	None
11	Pet. ether	H_2SO_4 KOH	None	2m x 4mm	5% OV-1 on Chromosorb W-HP	210	KOH

APPENDIX (cont'd)

Laboratory No.	Extraction Solvent	Clean-up Method	Pre-GLC Separation	GLC Column (length x bore, capillary underlined)	Column Packing	Column Temperature °C (* programmed)	Confirmation Method
13	Acetone/ Acetonitrile/ hexane	Silica	None	2m x 2mm	11% OV-17/QF-1	210	None
15	Hexane	Alumina	Silica	2m x 2mm	4% OV-1/6% OV-210 on Chromosorb W-AW-DMCS	220	None
16	Hexane	Alumina	Florisil	GCMS	No detail		GCMS
20	Hexane	Alumina	Silica	(1) 1.5m x 2mm	1.5% OV-1/1.95% QF-1 on Gaschrom Q	205	2 GLC columns
				(2) 1.5m x 2mm	5% QF-1/4% DC-200 on Chromosorb W-AW-DMCS		
21	Pentane	H_2SO_4	None	(1) 1.6m x 3mm	5% QF-1 on Gaschrom Q	180	MgO reaction column on GLC
				(2) 1.6m x 3mm	1.5% OV-17/2% QF-1 on Chromosorb W-AW-DMCS	195	
22	Hexane	Hexane/DMF, Alumina	None	1.5m x 3mm	1.5% SP-2250/ 1.95% SP-2401 on Supelcoport	205 and 230 (separately)	None
23	Hexane	H_2SO_4	Alumina, Silica	2m x 3mm	2.5% OV-1 on Chromosorb G-AW-DMCS	210	None (PCB only)
25	Pentane	Alumina	Silica	(1) 1.5m x 3mm	3% NPGS on Gaschrom Q	215	HCB, α- and γ-HCH PCB, dieldrin on (1)
				(2) 50m x 0.5mm	SE-30 (WCOT)	235	DDE, DDD, DDTs, HE, β - HCH on (2)
26	Pet. ether	Alumina	Silica	1.8m x 2mm	4 pts 3% OV-210 + 1 pt 3% OV-17 on Chromosorb W-HP	190	None
27	Pentane	KOH, Alumina	None	25m	SE-52 or SE-30	100-200 *	None
28	Hexane	Alumina	Silica	(1) 2m x 2mm	10% DC-200 + 7% QF-1 + 3% OV-225 on Chromosorb W-HP	205	None
				(2) 1m x 2mm	5% SE-30 on Chromosorb W-HP	200	None

APPENDIX (cont'd)

Laboratory No.	Extraction Solvent	Clean-up Method	Pre-GLC Separation	GLC Column (length x bore, capillary underlined)	Column Packing	Column Temperature °C (* programmed)	Confirmation Method
29	Hexane	Alumina	Silica	1.8m x ?	1.5% SP-2250/ 1.95% SP-2401 on Supelcoport	205	None
31	Hexane	H_2SO_4	None	(1) 20m x 0.25mm	OV-1	220	
				(2) 10m x 0.25mm	OV-101	?	GCMS
				(3) 60m x 0.25mm	OV-101	?	
32	Hexane	H_2SO_4	None	45m x ?	SE-54	100-230 *	KOH
34	Cyclohexane	H_2SO_4	Silica for Dieldrin	25m x 0.24mm	SE-54	70-210 *	KOH, silica column
35	Hexane	H_2SO_4	None	1.8m x 2mm (i.d.)	1.5% OV-17 + 1.95% OV-210 on Gaschrom Q	210	KOH
37	Hexane	Hexane/DMF Alumina	Alc. KOH Florisil	(1) 2m x ?	6% QF-1 + 4% SE-30 on Gaschrom Q	210	KOH
				(2) 2m x ?	10% DC-200 on Gaschrom Q	205	KOH
40	Acetone/hexane	H_2SO_4	Silica	3.7m x 1.8mm	7 pts 4% QF-1 + 3 pts 2% SF-96 on Chromosorb W-AW-DMCS	170-210 *	CrO_3, KOH
41	Hexane	Alumina	Silica	(1) 1m x 6mm (i.d.)	3% OV-17 on Chromosorb W-HP	185	None
				(2) 1.2m x 10mm (i.d.)	4% OV-101 on Chromosorb W-HP	230	None
42	Hexane	Alumina	Silica	(1) 1.5m x 2mm (i.d.)	3% dexsil 300 on Chromosorb W-AW-DMCS	200	GCMS
				(2) 1.5m x 2mm (i.d.)	3.8% SE-30 on Diatoport S	200	GCMS
44	Toluene/Ethyl acetate	Gel permeation	GPC, Florisil, Silica	1.8m x 2mm	1.5% SP-2250/ 1.95% SP-2401 on Supelcoport	190 (pesticides) 200 (PCB) 165-235 * (polar cpds)	GCMS

Indication of spine colours

Reports of the Advisory Committee on Fishery Management	Red
Reports of the Advisory Committee on Marine Pollution	Yellow
Fish Assessment Reports	Grey
Pollution Studies	Green
Others	Black

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