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INTERCOMPARISON EXERCISE ON THE ANALYSIS OF INDIVIDUAL CHLOROBIPHENYL CONGENERS IN MARINE MEDIA - FIRST STEP: OPTIMIZATION OF GAS CHROMATOGRAPHIC CONDITIONS

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Contents

Abstract.

In this report the results of the first step of the ICES/IOC/OSPARCOM intercomparison exercise on the analysis of chlorobiphenyl congeners in marine media are summarized. Results were received from 62 laboratories. An encouraging agreement is achieved, with standard deviations for the reproducibility of 1.11-1.12 for all CBs except CB 52 for a group of 47 laboratories. The optimization procedure of the gas chromatograph was experienced by many participants as a valuable learning process. This optimization of the GC conditions has led to a better level of agreement in comparison with former intercomparison exercises on CB analysis.

Difficulties were experienced with the identification of the linear range of the electron capture detector and bringing the unknown solution within this linear range. Results based on peak heights showed a better reproducibility than results based on peak areas. The separation of the CBs 28 and 31 was the most difficult one. Only 28 laboratories were able to achieve a separation for these two CBs.

It is concluded that the second step of this exercise may be organized. This step will involve in principle an analysis of a cleaned blubber extract and a cleaned sediment extract.

Introduction.

For more than 20 years the contamination of different environmental compartments with polychlorinated biphenyls (PCBs) has been one of the major sources of concern of institutes and organizations dealing with marine pollution problems. At the same time there have been problems with the comparability of the PCB analysis, which could not be solved until today. Efforts were made by ICES (International Coucil for the Exploration of the Sea) through conducting intercomparison exercises, at first based on total PCB-analysis (1,2,3) and later, when chromatographic techniques improved, with individual chlorobiphenyl congeners (2,3). The results so far obtained were not satisfactory.

Considering the growing concern about the effect of PCBs on marine organisms, an intercomparison exercise on the analysis of individual chlorobiphenyl congeners (CBs) was designed as a combined effort of ICES, IOC (Intergovernmental Oceanographic Committee) and OSPARCOM (Oslo and Paris Commissions).
Based on experiences of a CB intercomparison exercise which was conducted by the Community Bureau of Reference of the European Communities, a stepwise approach was chosen for this exercise.

Three steps were designed:

1) analysis of standard solutions
2) analysis of extracts
3) analysis of a sample of seal blubber

The objectives of this exercise were defined in the following way:

1) To determine the variation in the results of the analysis of chlorobiphenyls among the participating laboratories.
2) To identify the sources which can cause this variation.
3) To reduce this variation by means of a learning process through a step-by-step organized intercomparison exercise.

For the first step of the exercise, J. Duinker (Institut für Meereskunde an der Universität, Kiel) would act as coordinator on behalf of IOC and J. de Boer (Netherlands Institute for Fishery Investigations, IJmuiden) on behalf of ICES.
It was agreed that J. Calder (National Oceanic and Atmospheric Administration, Washington) would assist with the evaluation of the data of the OSPARCOM laboratories.
The statistical evaluation would be performed by J. v.d. Meer (Netherlands Institute for Sea Research, Texel), member of the ICES Working Group on Statistical Aspects of Trend Monitoring.

The following CBs were chosen to be used in this intercomparison exercise:

CB 28	- 2,4,4' - trichlorobiphenyl
CB 31	- 2,5,4' - trichlorobiphenyl
CB 52	- 2,5,2',5' - tetrachlorobiphenyl
CB 101	- 2,4,5,2',5' - pentachlorobiphenyl
CB 105	- 2,3,4,3',4' - pentachlorobiphenyl
CB 118	- 2,4,5,3',4' - pentachlorobiphenyl
CB 138	- 2,3,4,2',4',5' - hexachlorobiphenyl
CB 153	- 2,4,5,2',4',5' - hexachlorobiphenyl
CB 180	- 2,3,4,5,2',4',5' - heptachlorobiphenyl
CB 189	- 2,3,4,5,3',4',5' - heptachlorobiphenyl

Participants.

Ampoules and guidelines were sent to 90 laboratories. A complete list of the ICES and OSPARCOM participants is given in table 1. Two IOC laboratories returned results. They are included in table 1.

Materials and methods.

Each laboratory was provided with a set of 4 ampoules, containing:

A - a stock solution of the 10 CBs in iso-octane, concentrations: 750 ng/ml each,
B - a solution of the same CBs in an unknown concentrations plus some CBs of unknown identity,
C - a solution of octachloronaphtalene (OCN) in iso-octane, to be used as an internal standard,
D - a blank solution of iso-octane.

The purities of the CB stock solutions were >98% in ECD chromatograms but in FID chromatograms sometimes contaminants were apparent. It was advised to use these CB solutions only for this test and not for any other quantitative purpose. The basic question of the exercise was to determine the concentrations of 10 CBs in the B solution, using the A solution as a standard. The concentrations of the CBs in the B solution were 1/10 of the CB concentrations in the A ampoule with the exception of 52, which was about at the same level as the concentration in the A standard (791 ng/ml).

It was asked to analyze the solution on two columns of different polarity. One column should be a SE-54 column or a column with a comparable polarity to SE-54 (5% phenyl 95% dimethylpolysiloxane). The choice of the second column was left to the participants.

A number of suggestions were given in the guidelines. These suggestions concerned internal diameters and lengths of the capillary columns (preferably $\leq$0.25 mm i.d., $\geq$25 m long), carrier gas (hydrogen or helium), injection volume (fixed volume $\leq$1 µL, optimization of the injection system, the use of balances or syringes and the use of iso-octane for the preparation of dilutions.

A linearity test must be carried out with 8 different dilutions of the A solution for the CBs 52, 101 and 180. The internal standard, octachloronaphtalene (OCN), had to be added to the different dilutions. Linearity graphs had to be constructed and the linear range of the detector had to be identified.

Two dilutions from the linearity series had to be chosen, bracketting the concentrations of the CBs in the unknown B solution. The internal standard OCN had to be added to the unknown. During each of 6 days, 3 days per column, the blank D, two A standards and the unknown B must be injected.

It was asked to quantify the concentrations of the 10 CBs in the B solution by using peak heights and peak areas. Furthermore 4 unknown CBs had also been added to the B solution. As an optional exercise, participants were asked to identify and quantify the added unknown CBs with their own standards.

Results.

Results were received from 62 participants, which is 69% of the total numer of laboratories which initially agreed to take part in this exercise. Not all results were received before the official deadline of 30 June 1989. A considerable number of laboratories reported a delay, because of different problems with their equipment. This shows that many laboratories have problems to bring or to keep their equipment in good condition. Results were accepted until 10 November 1989. Together with the results a variety of remarks were returned to the co-ordinators, concerning for example: the use of a different internal standard, difficulties with the equipment like bleeding, detector stability, use of different solvents, etc. Some laboratories only produced results on one column. All results and chromatograms were carefully examined by the co-ordinators. Next to a "chromatographic" observation, a statistical evaluation was performed.

Statistical evaluation.

The statistical evaluation was partly based on the international standard ISO 5725 for interlaboratory tests (4). According to this standard the repeatability value r and the reproducibility value R were calculated.
The repeatability value r is the value below which the ratio of two single test results (maximum/mimimum) obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory, and a short interval of time) may be expected to lie with a probablity of 95%. The reproducibility value R is the value below which the ratio of two single test results obtained with the same method on identical test material, under different conditions (different operators, different apparatus, different laboratories and/or different time), may be expected to lie with a probability of 95%.

Because the error in this exercise appeared to show a relative character, in contravention of the ISO standard, a model with a multiplicative error structure was used. After log-transformation and back transformation the model provided standard deviations for the repeatability (Sr) and reproducibility (SR) which must be applied as factors instead of using them as coefficients of variation. An Sr of e.g. 1.22 means that in a next intercomparison exercise the values are expected to be in an area of the mean divided by 1.22 - the mean multiplied by 1.22 with a probability of 68%. For small Srs and SRs the values Sr-1 and SR-1 may roughly be compared with the values of the coefficients of variation CV(r) and CV(R) which are mostly calculated for intercomparison exercises. Table 2 shows the results of r, R, Sr and SR for this exercise. Recall that the relations between r and Sr and R and Sr are resp. 2.8 log Sr = log r and 2.8 log SR = log R. For each CB, laboratory means with prediction intervals are shown in the figures 1-10. Figure 11 shows an overall picture of a principal component analysis. This figure summarizes the findings of the statistical analysis. Outlying laboratories are easily detected.

Discussion.

With 62 participating laboratories, this intercomparison exercise is probably the biggest ever organized for chlorobiphenyl analysis. The large number of participants shows also that in recent years more laboratories have started with capillary chromatography. This technique is necessary for the analysis of individual CBs.

The design of this intercomparison exercise was clearly different from former exercises. In the first place a stepwise approach was chosen. This approach had shown to be

successful in intercomparison exercises conducted by the Community Bureau of Reference of the European Communities (BCR) (5).
Therefore in this first step only standard solutions were provided, just for the intercomparison of the GC analysis. Secondly all participants were asked to optimize their GC conditions before starting the analysis. Advice was given for optimization of injector and detector temperatures, temperature programs, determination of the linear range of the detector, etc. The optimization procedures cost relatively much time compared with the time of analysis. This may have deterred some participants.

Table 2 shows a summary of the results. It appears that the mean SR for all CBs except CB 52, is 1.23 with a range of 1.18 - 1.29 (table 2a). The results of one laboratory were left out the statistical evaluation, because of very deviating figures. Next to this laboratory, 10 other laboratories were identified as outliers (Figure 11). Without these laboratories the mean SR without CB 52 is 1.11 - 1.12 (table 2b).

A rather large group of laboratories was not able to determine the CBs 28 and 31. These laboratories generally produced slightly less precise results for the other CBs. Therefore 28 laboratories (without the 10 outliers) which had determined all CBs were selected for which the Sr and SR were calculated. The mean SR for this group of selected laboratories is 1.12 (range 1.11-1.13), without the CBs 52 and 118.

The first round of the BCR intercomparison exercise (6), also conducted only with standard solutions (7 CBs), resulted in coefficients of variation for the reproducibility CV(R)s of 5.5 -17.7% (mean 10.4%). However, this BCR-exercise was performed by a group of 14 selected laboratories, all with experience in CB analyses. Besides, in the BCR-test the internal standard was already added to the ampoules, which may have reduced the CV(R) in comparison with the ICES/IOC/OSPARCOM exercise.
Other intercomparison exercises mostly have been carried out with fat extracts or fish oils, which makes the comparison more difficult. CVs in ICES 5th intercomparison exercise (11 CBs) ranged from 9-98% (mean 39%) (2). CVs in the ICES intercomparison exercise of CBs in Baltic herring oil (11 CBs) ranged from 13-109% (mean 37%) (3). A recent IAEA intercalibration exercise of CBs in tuna homogenate (6 CBs) showed CVs from 15-88% (mean 41%) (7).

The results show that for the analysis of the CBs 101, 105, 153, 138, 180 and 189 no major problems were encountered. However, this does not mean that for a normal practice sample the same agreement will be achieved. In this case only a clean standard solution had to be analysed. For example the presence of CB 132 will hinder the analysis of CB 105 in environmental samples. Therefore it is emphasized that for the next step column lengths should be around 50 m and internal diameters should not exceed 0.2 mm.

Only 28 laboratories were able to quantify the CBs 28 and 31. Of all separations this is the most difficult one. Non-polar stationary phases will provide better results.

Fig. 3 shows the results of CB 52. The results obtained for this CB were the worst, with a mean deviating 25% from the true value and a SR of 1.43 for all results (table 2a). There are two reasons for this bad performance: 1) the concentration in the B solution was 10 times higher than the concentration of the other CBs, 2) the close eluting CB 49 was added as an unknown, also in a very high concentration (table 3).
Although this situation with very high concentrations of only 1 or 2 CBs doesn't occur normally, it is striking that almost all participants had problems with this determination. The best way of analysis would have been an extra dilution of the B solution, bringing the concentration of CB 52 in the linear rang of the ECD. From the results of other intercomparison exercises (4,5) it may be expected, however, that with normal concentrations the results for CB 52 will be comparable with those of other CBs.

Figure 6 shows the results of CB 118. By adding CB 149 in a 20-fold concentration, an extra obstacle was put in the analysis of CB 118. The SR for all results of CB 118, 1.24,

is not very deviating from most other SRs, but it is based on a much smaller group of laboratories. This means that this small group has a good mutual agreement with a very acceptable mean of 75.1. Most of the other laboratories quantified the peaks of the CBs 118 and 149 together as CB 118, resulting in very high concentrations. For a normal practice sample it is expected that CB 118 can be quantified by most of the participants, possibly with a slightly higher SR. SE-54-like columns and more polar columns are suitable for the separation of the CBs 118 and 149.

CBs 49, 77, 110 and 149 had been added as unknown to the B solution. The participants were asked to identify and quantify these CBs. 24 Laboratories were able to identify CB 49, 23 laboratories identified correctly CB 149, 15 laboratories identified CB 110 and 15 laboratories identified CB 77. Only 8 laboratories were able to identify both CB 77 and CB 110. These two CBs coelute on a SE-54 column. Table 3 shows the results of the quantitative analysis. With a criterion of ± 25% deviation from the mean we arrive at 11 laboratories being able to quantify CB 49. 9 Laboratories quantified CB 149 correctly, 4 laboratories CB 110 and only 3 laboratories were able to quantify CB 77. The identification and quantification were performed with laboratory's own standards. Considering the mean results of the laboratories without the outliers, these laboratory standards apparently have a reasonable agreement.

Many problems were encountered in the identification of the linear range of the electron capture detector. By most laboratories a linear range for the CBs was found between 50 and 400 pg. This shows that there is a large gap between the information on linearity of ECDs supplied by gas chromatography firms, 4 to 5 decades, and the linearity which is found in practice, 1 decade at most. Especially below 50 pg there is a considerable deviation in the linearity of the ECDs. Unfortunately many participants injected quantities below 50 pg, even when they had identified a linear range above 50 pg. On the other hand, the disappointing results for CB 52, present in a much higher concentration than the other CBs, show that also in the higher range considerable errors are made. The conclusion of this test may be that it is emphasized to work in the linear range of the detector by concentration or dilution of the sample. If this is not possible by lack of enough sample material or in a situation with very low concentrations of the concerning compounds, a multi-level calibration is necessary for an accurate measurement.

The SE-54 or SE-54 like stationary phases were found to acceptable for the determination of the used CBs, providing the proper dimensions are used (8). Non-polar columns will be better suitable for the separation of 28 and 31, while more polar columns will be more suitable for the separation of the CBs 118 and 149.
Recent developments in stationary phases, e.g. those based on a different principle, like liquid cristalline phases (9), can possibly provide broader possibilities for the analysis of CBs. Multi-dimensional gas chromatography (9, 10) may also provide solutions for separation problems in CB analysis.

Positive identifications of CBs in the blank solution were reported by many participants. Concentrations upto 10% of the CB concentrations in the B solution were regularly reported, in exceptional cases even concentrations of 40 pg/µl were found in the C ampoule. This shows that background contamination, even only in the stage of injecting standard solutions is a severe problem for many laboratories. It is advised that participants check the purity of their solvents and cleanliness of syringes and glassware before starting with the analyses for the next step. Another source of contamination may be the septa of autosampler vials. Through the vapour inside these vials contaminants from the septa may be extracted.

Figure 11 shows that except for the group of outliers no dominating effects are present, caused by either the injection technique or column diameter employed.

Table 2d shows the Sr and SR for two CBs, calculated on the peak area results. The reproducibility is clearly worse, compared with the peak heights method with SRs of

1.27 and 1.30 for respectively CB 101 and CB 180 for the peak area method and respectively 1.23 and 1.21 for the peak heights method. Apparently the use of different integrators results in a worse reproducibility, compared with peak height calculation.

A few laboratories produced results obtained by GC - mass spectrometry. These results in general deviated from the ECD-results. Also a broad variation in the results was shown.

Conclusions.

a) The first step of the ICES/IOC/OSPARCOM intercomparison exercise on CB analysis has resulted in an encouraging agreement among a majority of the participants, with between group standard deviations of 1.10 - 1.13 for all CBs except CB 52. A group of 11 laboratories was identified as an outlier group for which reconsideration of the optimization process is advised.

b) This exercise has made clearly visible that major difficulties are met in identifying of the linear range of the electron capture detector and bringing the concentrations of the samples into this linear range.

c) Providing that the group of outlying laboratories will pay extra attention to the optimization of their GC conditions, it is recommended by the coordinators that the next step of this intercomparison exercise be organized.

d) Although a good separation of most CBs was obtained by most participants in this exercise, it must be emphasized that this is not a guarantee for an acceptable analysis of real samples. Especially for CB 105, but also for the other CBs one must be aware of close eluting or even coeluting peaks. The fact that only 3 laboratories were able to quantify the CBs 110 and 77 is clear warning against exaggerated optimism.

e) Capillary columns with chemically bonded 5% phenyl 95% dimethylpolysiloxane stationary phases have been shown to be suitable for this kind of analysis, when used under the proper conditions and with the proper dimensions. All other stationary phases, which were used in this study, were suitable for providing additional information.

f) The separation of the CBs 28/31 could only be obtained by approximately one half of the participants.

g) The separation of the CBs 118 and 149 is expected to be achievable by most participants, unless one of these CBs is present in much higher concentration than the other.

h) A significant difference in results between the peak area method and the peak height method was observed, with a worse reproducibility for the results based on peak areas.

i) Positive identifications of CBs in the blank solution were reported by many participants, in some cases up to 60% of the CB concentrations in the B solution. This shows that background contamination is present at many laboratories, even already in a stage where extraction and clean-up are not concerned.

j) Careful optimization of the GC conditions is essential before starting a CB analysis.

Acknowledgements.

The coordinators like to thank all participants for their kind cooperation and many useful comments. The comments of Dr. D.E. Wells, Dr. R. Misra, Dr. J. Uthe on the design of the exercise and the assistance of Dr. S. Wilson are gratefully acknowledged.

References.

1. Uthe, J.F., C.J. Musial, K.H. Palmork (1981), ICES CM 1981/E:49.

2. Uthe, J.F., C.J. Musial (1983). ICES CM 1983/E:38.

3. Reutergårdh, L., K. Litzén (1985). ICES MCWG 1988/7.2.3./1.

4. International Organization for Standardization (1986). Precision of test methods - Determination of repeatability and reproducibility for a standard test method by inter-laboratory test. ISO 5725.

5. Wells, D.E., J. de Boer, L.G.M.T. Tuinstra, L. Reutergårdh, B. Griepink (1988). Improvements in the analysis of chlorobiphenyls prior to the certification of seven CBs in two fish oils. Fresenius Z. Anal. Chem., 332, 591-597.

6. Tuinstra, L.G.M.T., A.H. Roos, G.A. Werdmuller (1983). BCR ringtest of individual chlorobiphenyls. RIKILT report 1983-05-26, Wageningen, The Netherlands.

7. Villeneuve, J.P., L.D. Mee (1989). Chlorinated hydrocarbons in tuna homogenate IAEA-351: Results of a world wide exercise. ILMR intercalibration exercise report no. 44, Monaco.

8. De Boer, J., Q.T. Dao (1989). The analysis of individual chlorobiphenyl congeners in fish extracts on 0.15 mm ID capillary columns. J. High Resolut. Chromatogr., 11, 755-759.

9. Guenther, F.R., S.N. Chessler, R.E. Rebbert (1989). The analysis of polychlorinated biphenyls by multidimensional gas chromatography. Proceedings of the 10th International Symposium on Capillary Chromatography, Riva del Garda, Italy, 666.

10. Schulz, D.E., G. Petrick, J.C. Duinker (1988). Chlorinated biphenyls in North Atlantic surface and deep water. Marine Pollut. Bull., 19 (10), 526-531.

Table 1 : Participants.

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54	FRUK	R.	Wijness	Forth River Purification Board	Colinton dell House, Westmill road	Colinton, Edinburgh EH 130 PH	UK
55		J.	MacAulay	Strathclyde Regional Council Chemists Department	8 Elliot Place	Glasgow	UK
XX		J.	Webster	Lothian Regional Drainage Dept.	Musselburgh Road, Leith	Edinburgh	UK
				Seafield Sewage Works			
57		D.A.	Kurtz	Pesticide Research Laboratory	The Pennsylvania State University	University Park, PA 16802	USA
58		C.S.	Peven	Battelle Ocean Sciences	397 Washington Street	Duxbury, MA 02332	USA
59		T.	Wade	GERG Texas A&M University	10 S. Graham Road	College Station, TX 77840	USA
XX		U.	Varanasi	NWAFC / NOAA	2725 Montlake Bvld. East	Seattle, WA 98112	USA
61		J.R.	Clayton	Science Applications Int. Corporation	4224 Campus PT. Court MS 210	San Diego, CA 92121	USA
62		C.	Younghans-Haug	UCSC-CDFG, Trace Organics Faulity	100 Shaffer Road	St. Cruz, CA 95060	USA
63		R.E.	Rebbert	NIST, Org. Anal. Research Devision	Center for Anal. Chemistiy	Gaithersburg, MD 20899	USA
64		J.W.	Farrington	University of Massachusetts-Boston	Harbor Campus	Boston, MA 02125-3393	USA
66		T.	Hillebrand	Netherlands Institute for Sea Research	Postbus 59	1790 AB Den Burg, Texel	The Netherlands

LAB. NO.	CODE	INI-TIALS	NAME	INSTITUTE	ADDRESS	CITY	COUNTRY
67		M	de Bie	Lab. ECCA, PVBA	Klaartestraat 24	B-9710 Zwijnaarde	Belgium
68		A.	v.d. Zande	RIN	Postbus 9201	6800 HB Arnhem	The Netherlands
69	VETN	A.	Polder	Veterinærinstituttet	Posboks 8146 Dep.	0033 Oslo 1	Norway
70		D.F.	Gadbois	NOAA / NMFS,Gloucester Lab.	30 Emerson Avenue	Gloucester MA 01930	USA
XX		P.	Boehm	Arthur C. Little Inc.	Acorn Park	Cambridge MA 02140	USA
72		J.	Nieuwenhuizen	Delta Instituut	Vierstraat 28	4401 EA Yerseke	The Netherlands
73		O.	Anderson	Swedish National Food Administration	Box 622,	S-751 26 Uppsala	Sweden
				Food Research Department			
74		V.	Tulchinsky	Institute of applied ecophysics	Coscomhydromet, Glebovskaya 20 B	Moscow 107258	USSR
76		A.V.	Botello	Instituto de ciencias del Mary y Limnologia	Apartado Pastal 70-305	Mexico City	Mexico
77		Z.	Jiayi	Institute of Marine Environmental Protection	P.O. Box 303	Dalian	China
				State Oceanice Administration			

Table 2. Summary of results.

a) All results (based on peak heights).

CB	k	n	mean	r	R	Sr	SR
28	43	189	71.9	1.256	1.708	1.08	1.21
31	41	175	75.1	1.259	1.593	1.09	1.18
52	48	235	592	1.383	2.738	1.12	1.43
101	55	286	81.2	1.291	1.799	1.10	1.23
105	54	280	69.8	1.289	1.825	1.09	1.24
118	34	159	75.1	1.489	1.822	1.15	1.24
138	55	286	70.3	1.293	1.726	1.10	1.22
153	53	276	76.9	1.315	2.025	1.10	1.29
180	55	286	70.1	1.277	1.705	1.09	1.21
189	55	285	70.5	1.299	1.895	1.10	1.24

b) Results without outliers (based on peak heights).

CB	k	n	mean	r	R	Sr	SR
28	37	164	73.5	1.245	1.377	1.08	1.12
31	36	156	75.6	1.253	1.379	1.08	1.12
52	39	204	592	1.141	2.378	1.12	1.36
101	45	243	84.6	1.280	1.382	1.09	1.12
105	44	237	72.8	1.274	1.365	1.09	1.12
138	45	243	72.8	1.284	1.348	1.09	1.11
153	43	233	81.6	1.303	1.382	1.10	1.12
180	45	243	71.5	1.263	1.334	1.09	1.11
189	45	243	72.0	1.285	1.360	1.09	1.12

c) Selected results (based on peak heights).

CB	k	n	mean	r	R	Sr	SR
28	28	120	73.7	1.236	1.372	1.08	1.12
31	28	118	76.2	1.253	1.414	1.08	1.13
52	28	150	597	1.276	1.733	1.09	1.22
101	28	153	83.6	1.244	1.339	1.08	1.11
105	28	153	72.3	1.231	1.319	1.08	1.10
138	28	153	72.4	1.254	1.324	1.08	1.11
153	28	152	81.8	1.261	1.367	1.09	1.12
180	28	153	71.8	1.233	1.331	1.08	1.11
189	28	153	72.5	1.264	1.397	1.09	1.13

d) All results (based on peak areas)

CB	k	n	mean	r	R	Sr	SR
101	56	286	83.2	1.330	1.973	1.11	1.27
180	56	284	73.5	1.297	2.100	1.10	1.30

k: number of laboratories
n: total number of observations

Table 3. Quantification of the additional CB's 49, 77, 110 and 149 (pg/µl)

LAB. NO.	CB 49	CB 77	CB 110	CB 149
	x ± s.d.-n	x ± s.d.-n	x ± s.d.-n	x ± s.d.-n
7	1574 ± 404 - 12		140 ± 20 - 12	931 ± 230 - 12
14				1396 ± 133 - 12
21	1666 ± 204 - 12		130 ± 91 - 12	1363 ± 141 - 12
39	1460 ± 49 - 12			1518 ± 61 -6
35	1367 ± 107 - 12	50 ± 3 - 6	102 ± 8 - 6	1425 ± 97 - 12
36	1231 ± 31 -12	52 ± 2 - 6	109 ± 3 - 6	1458 ± 38 - 9
39	739 ± 208 - 12	368 ± 84 - 12		2100 ± 179 - 6
43	1739 ± 88 - 12		114 ± 7 - 12	1659 ± 92 -12
45	1236 ± 84 - 12			1356 ± 97 -12
47	1200 ± 98 - 12	234 ± 31 - 12		
50	1651 ± 54 - 12			1415 ± 61 - 12
63	1536 ± 20 - 6	60 ± 4 - 7		
73	1766 ± 112 - 2	98 ± 0 - 2	108 ± 0 - 1	1468 ± 0 - 1
mean	1493 ± 209 - 11	54 ± 5.3 - 3	108 ± 4.9 - 4	1450 ± 93 - 9
real conc. :	1500	60	100	1500

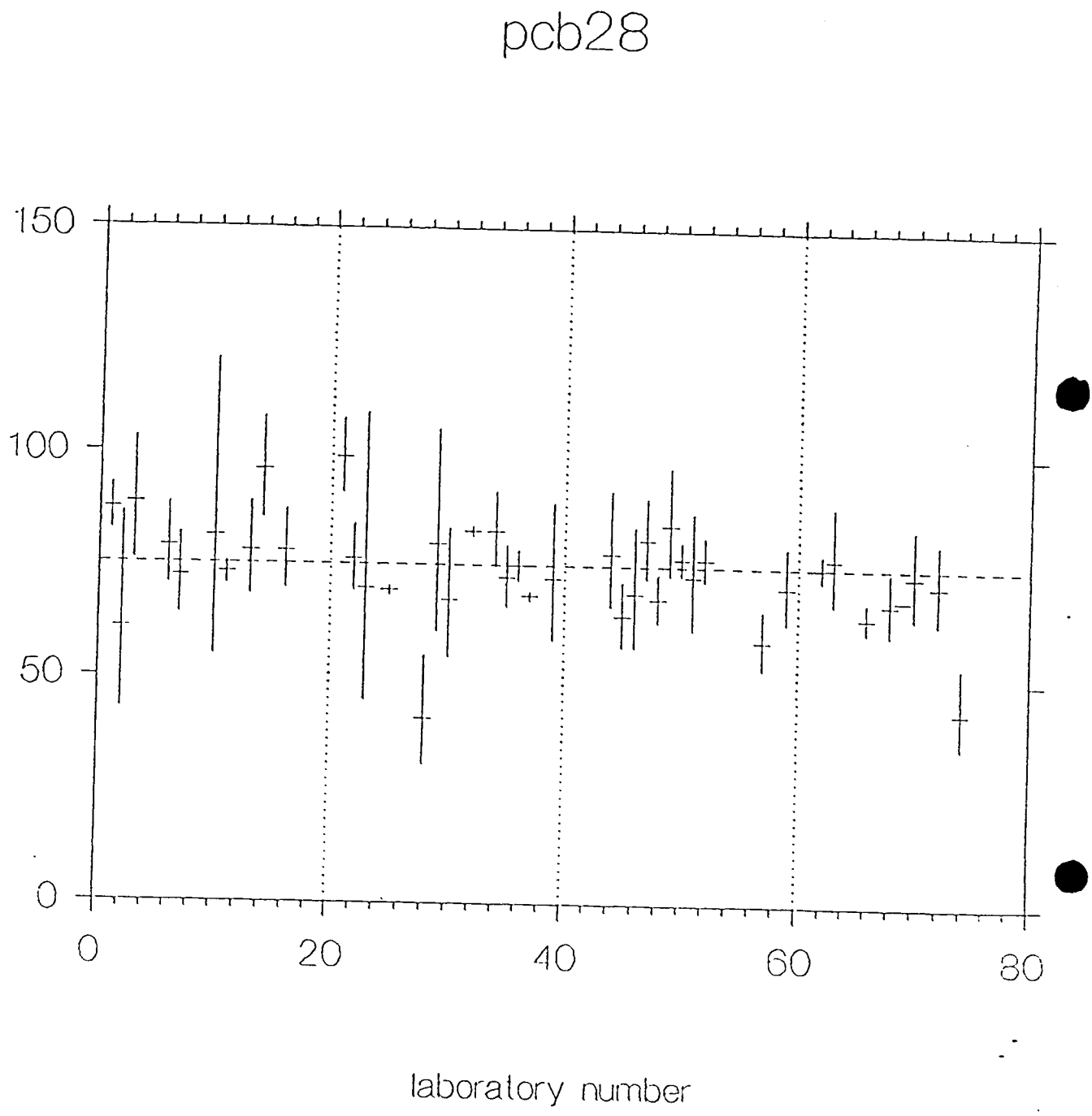

Figure 1 Results of CB 28. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

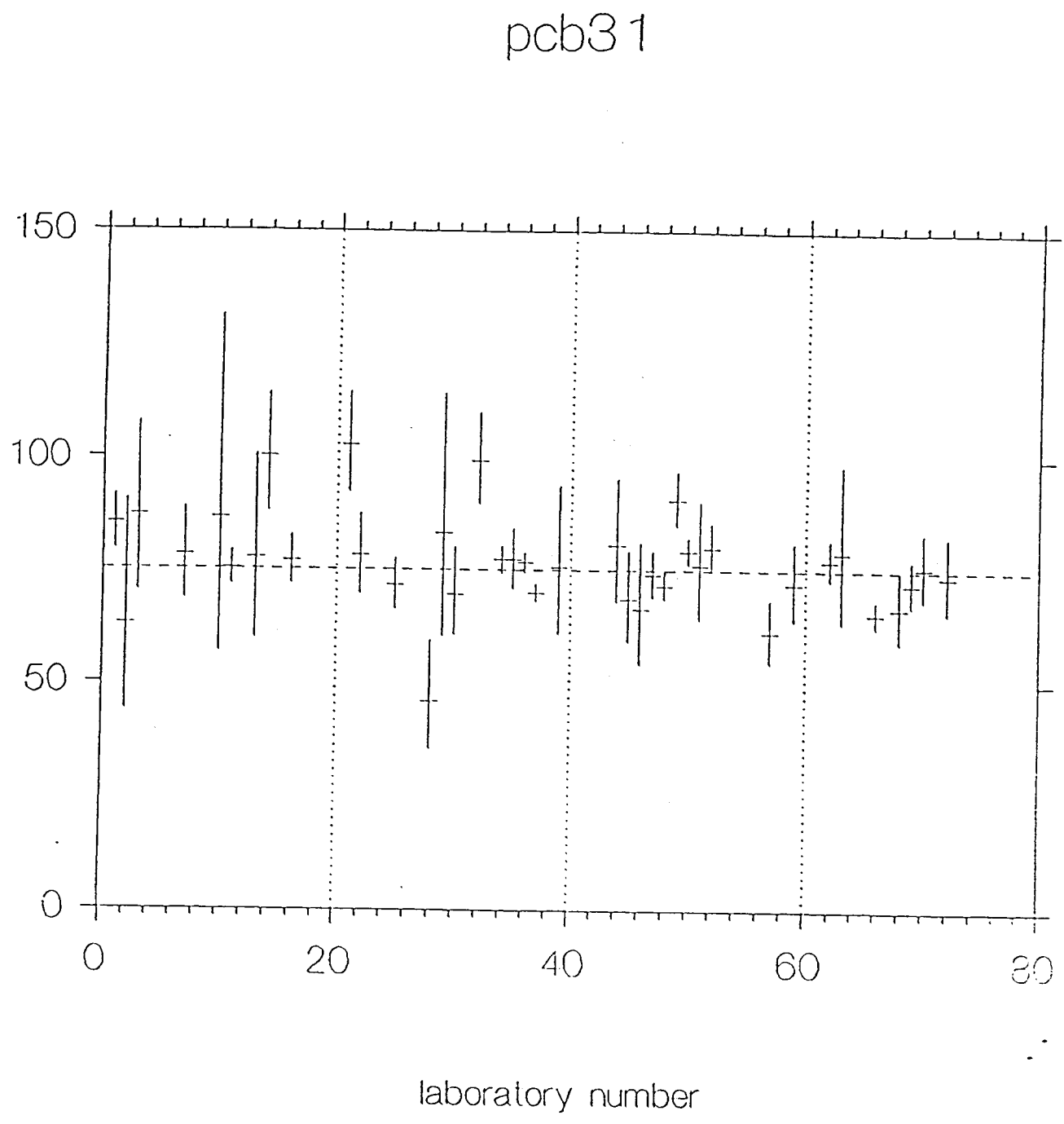

Figure 2 Results of CB 31. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

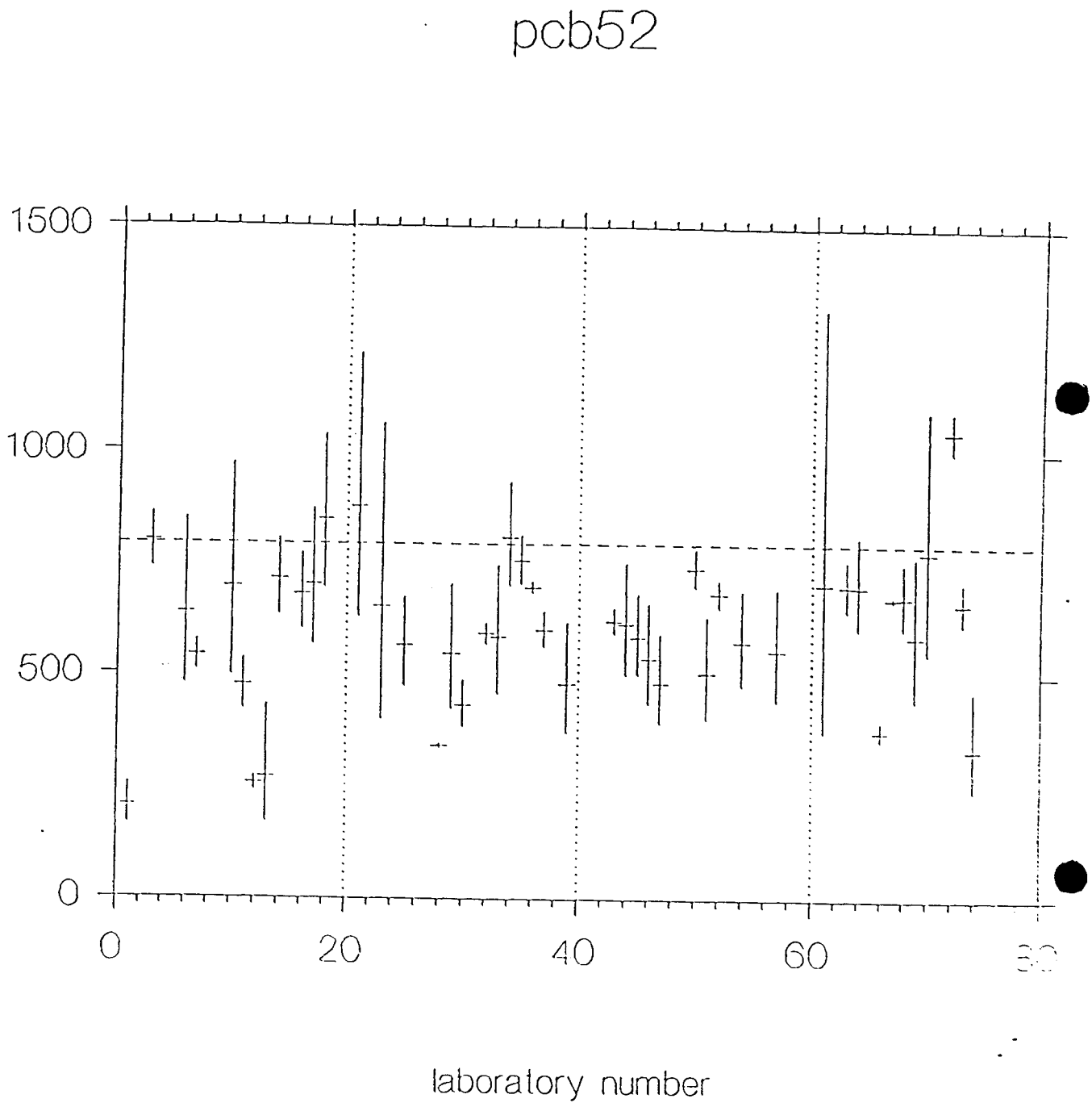

Figure 3 Results of CB 52. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

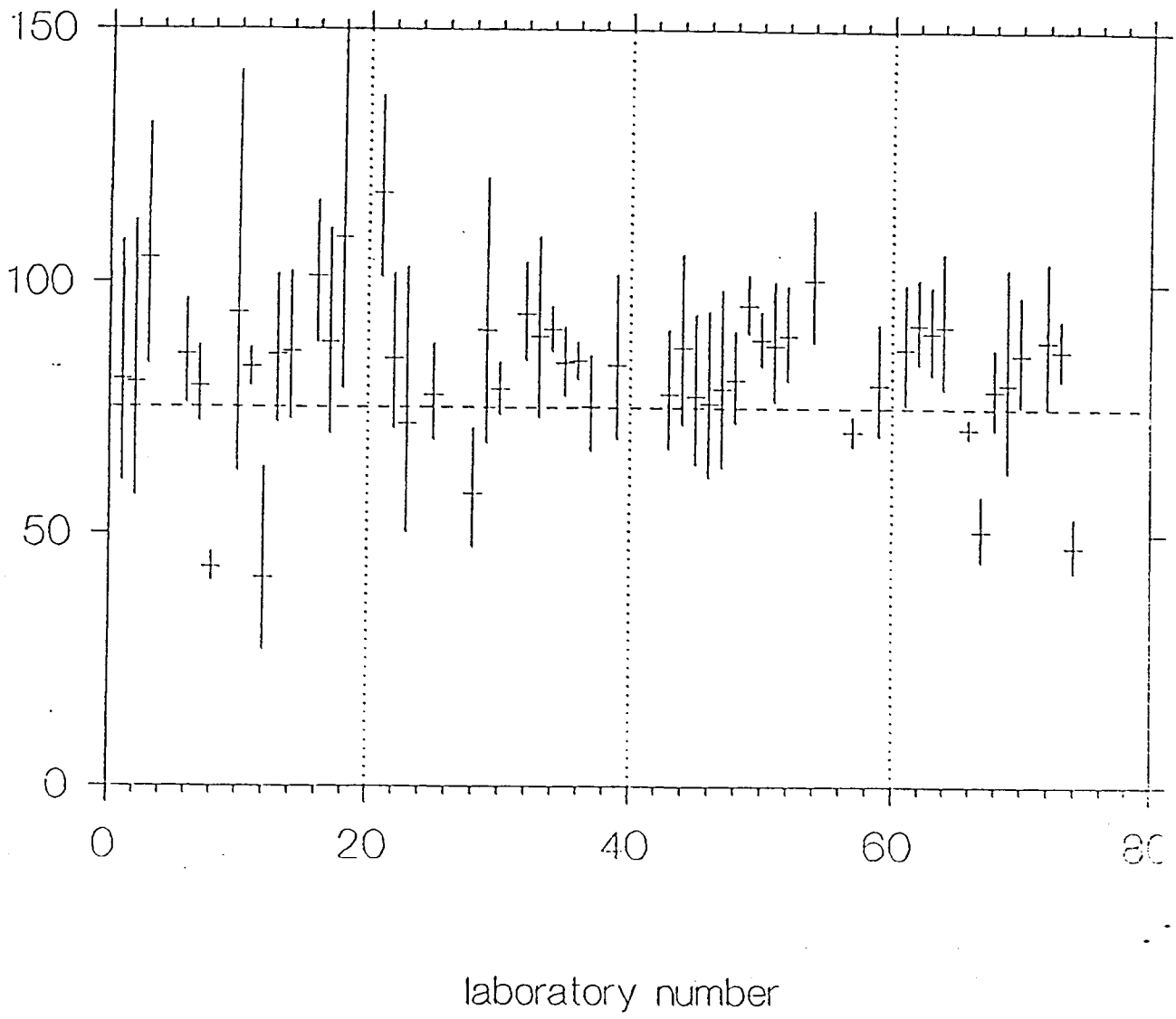

Figure 4 Results of CB 101. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

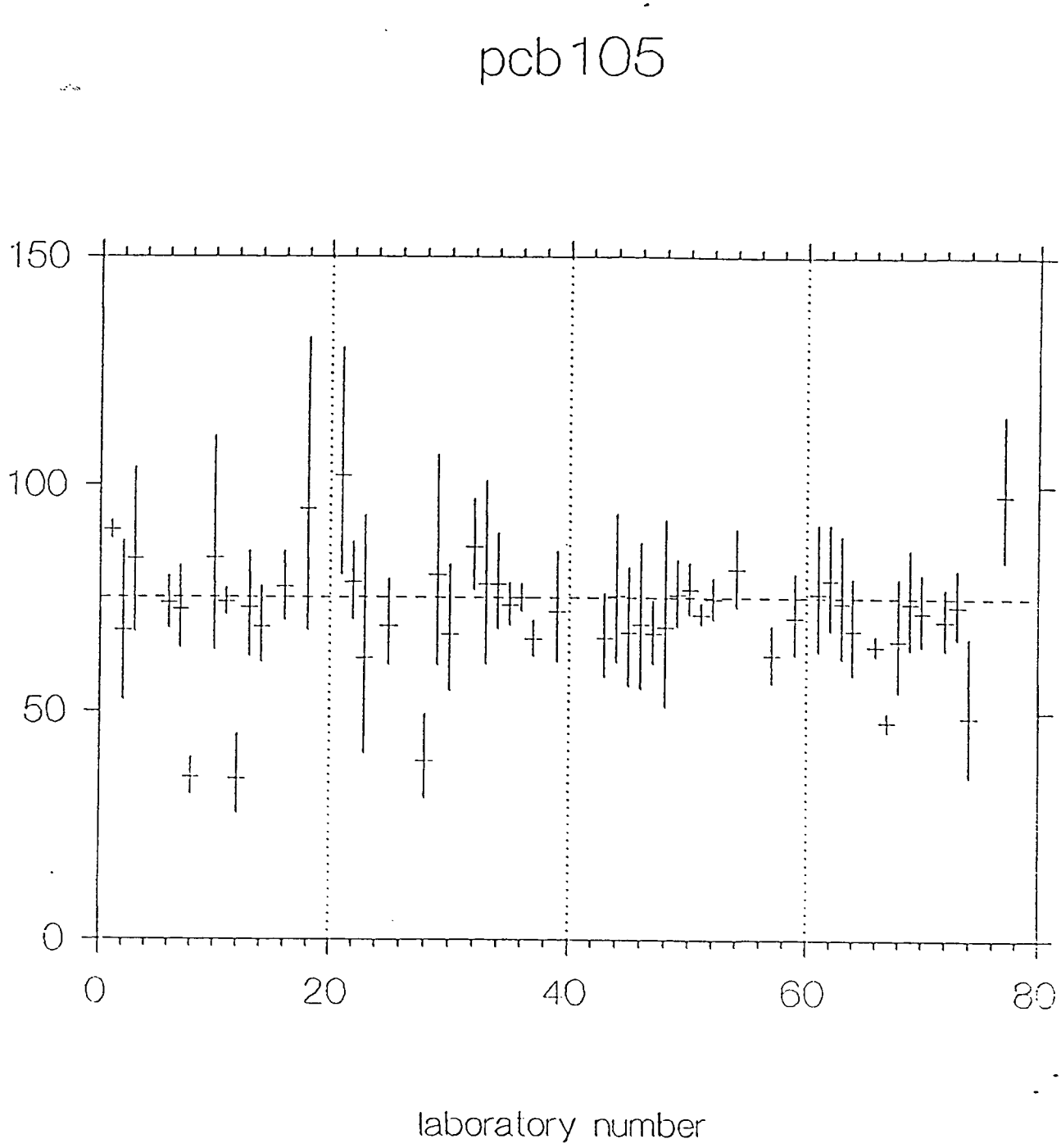

Figure 5 Results of CB 105. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

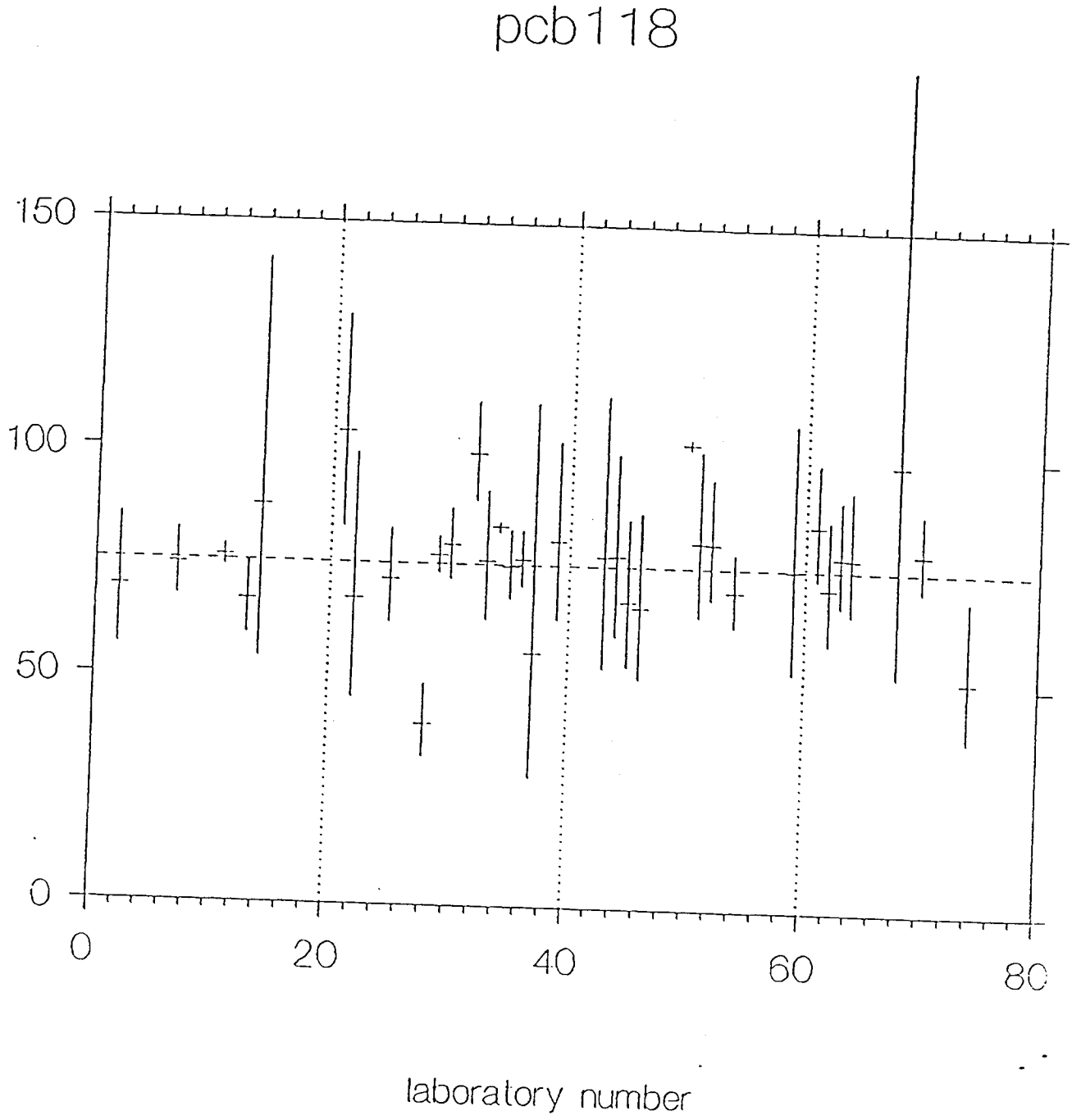

Figure 6 Results of CB 118. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

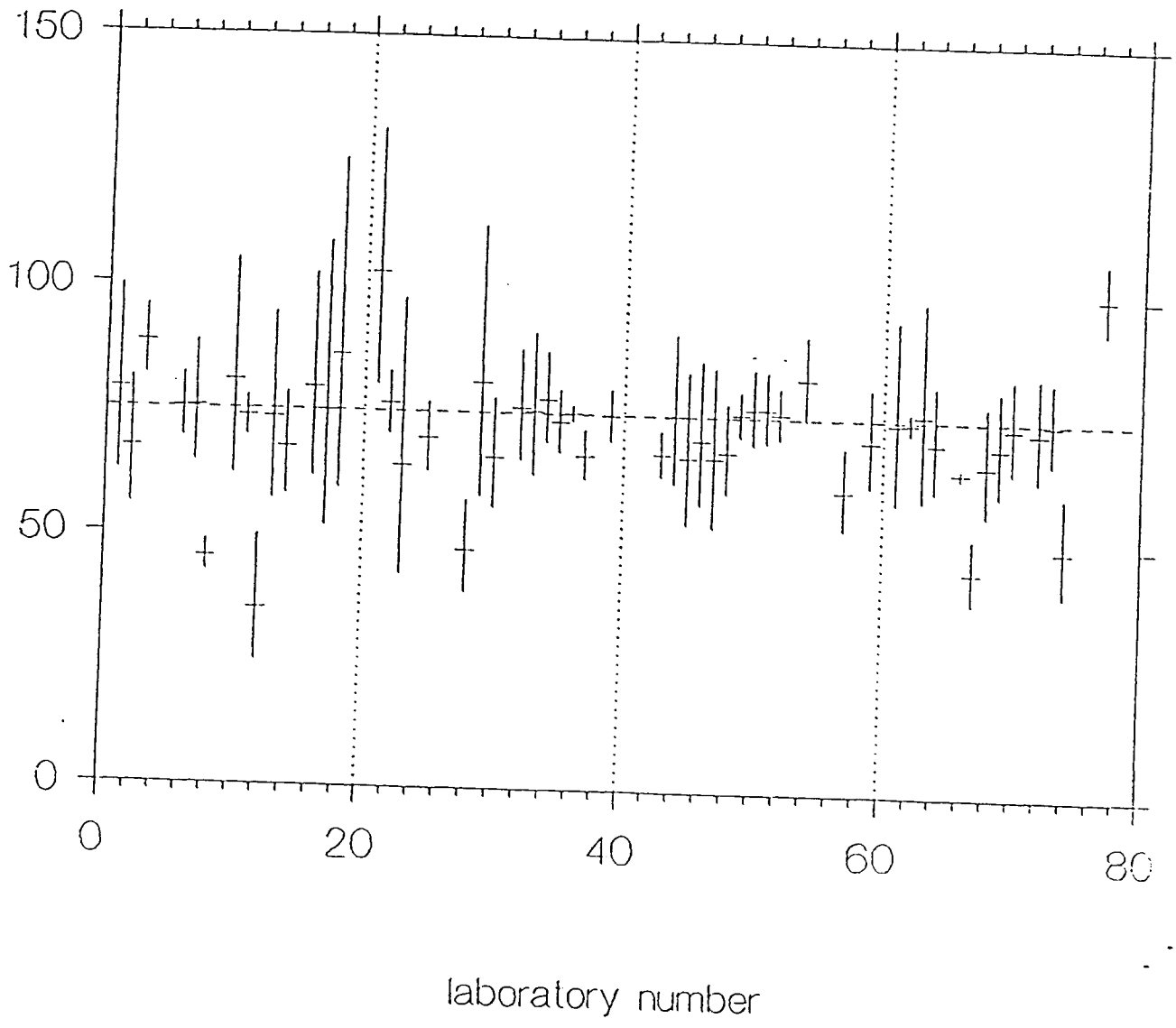

Figure 7 Results of CB 138. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

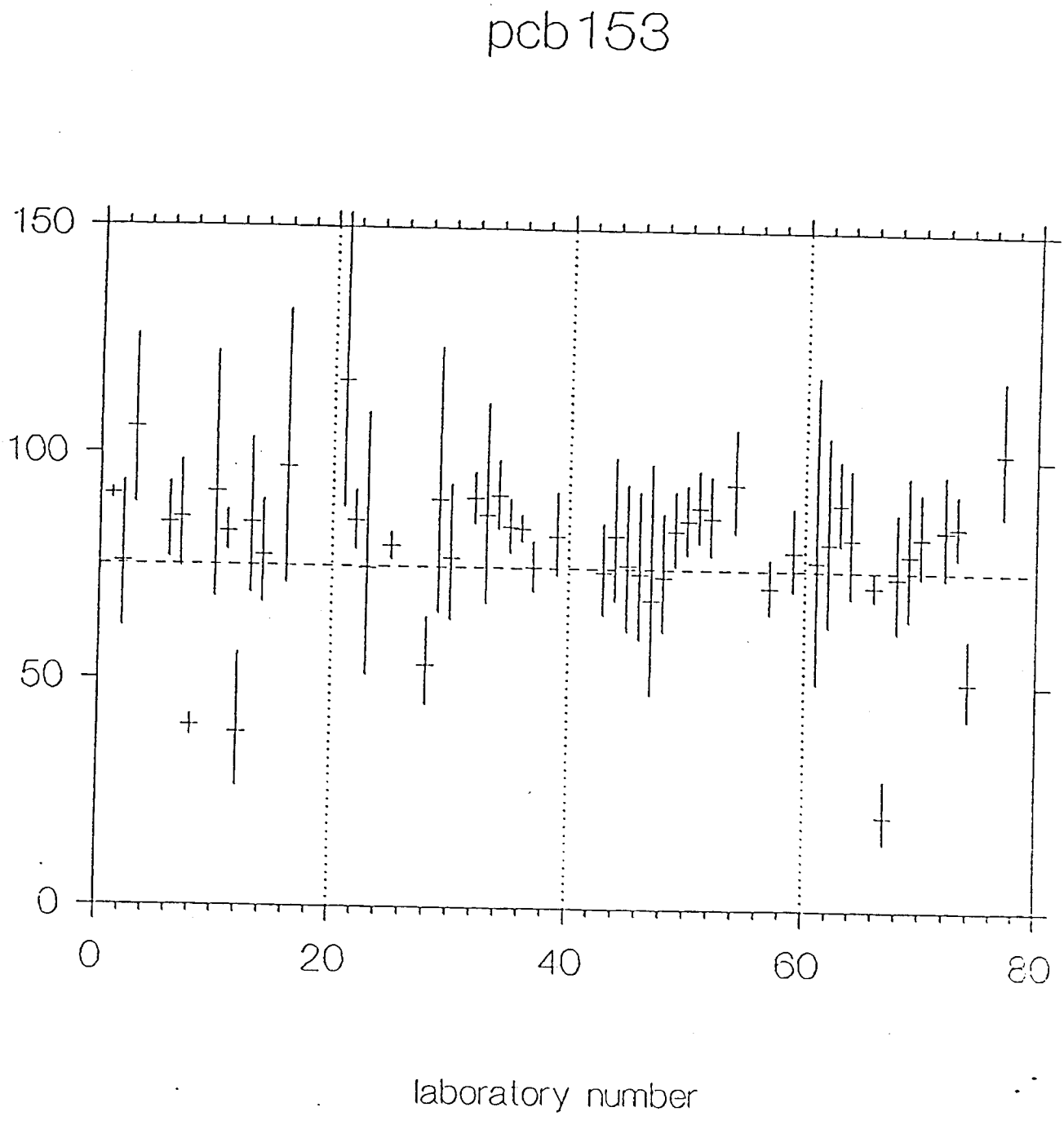

Figure 8 Results of CB 153. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

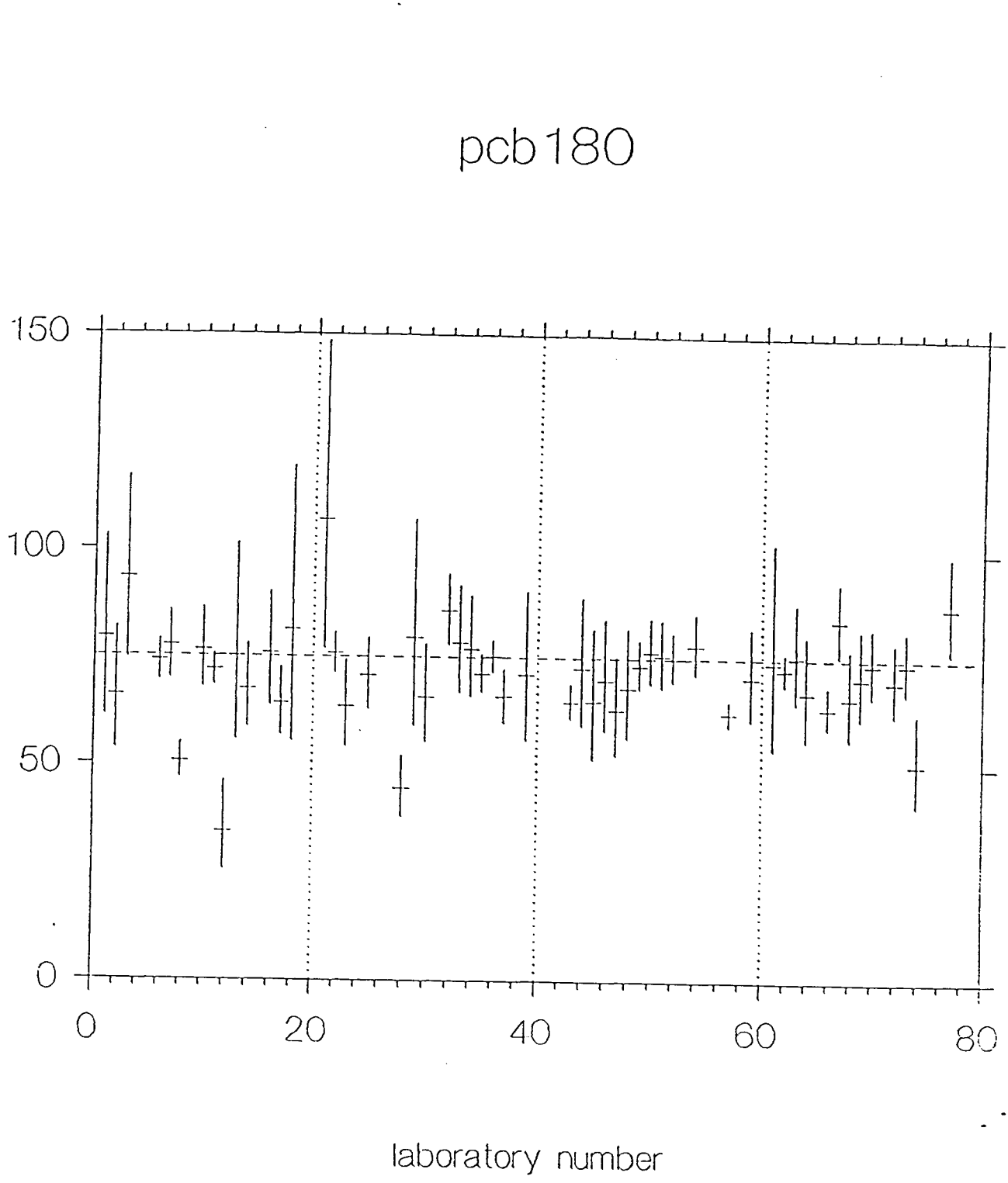

Figure 9 Results of CB 180. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

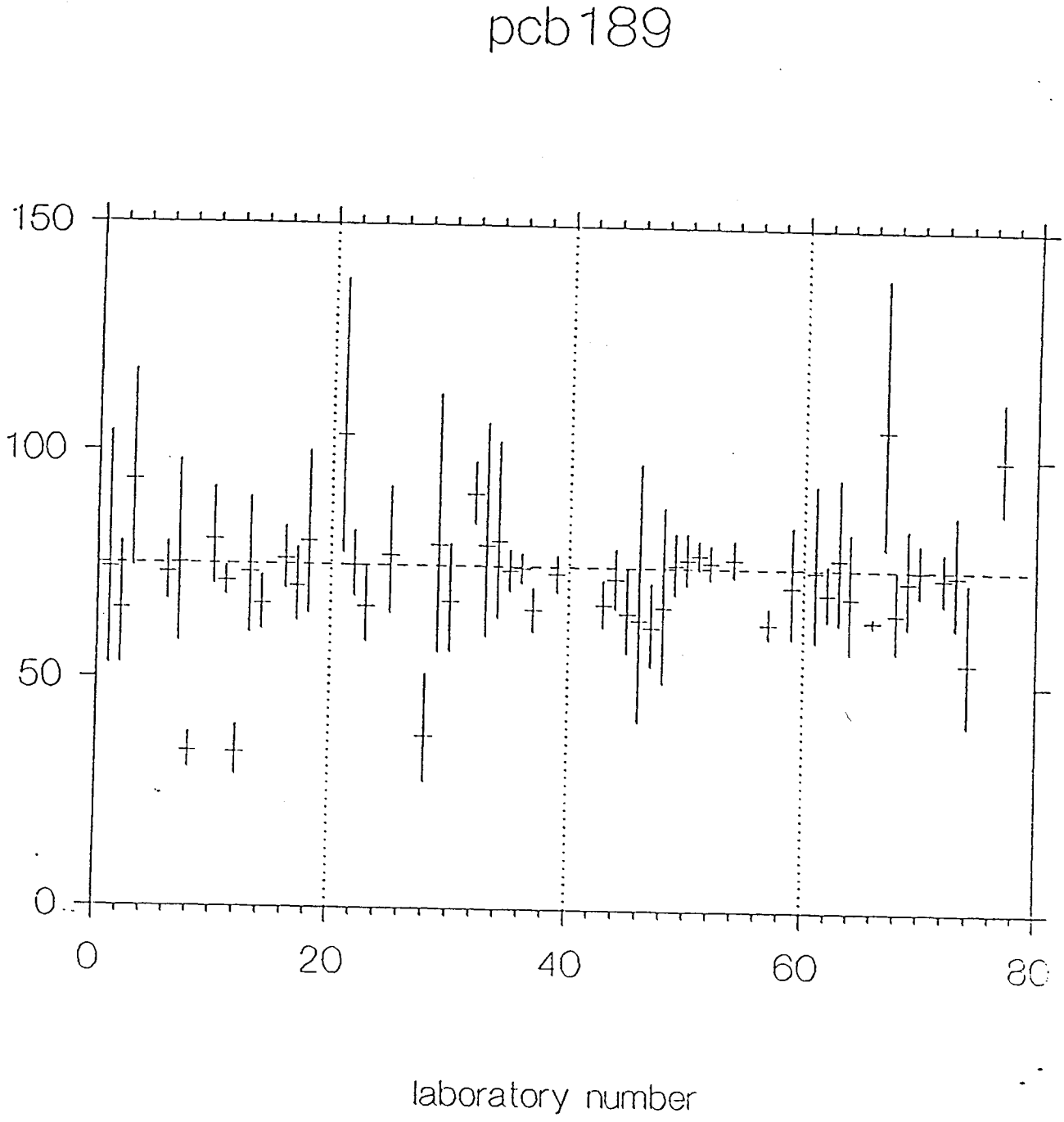

Figure 10 Results of CB 189. Mean concentrations with 95% prediction-interval (twice the standard deviation of the observations) versus the laboratory number. The broken horizontal line shows the true value.

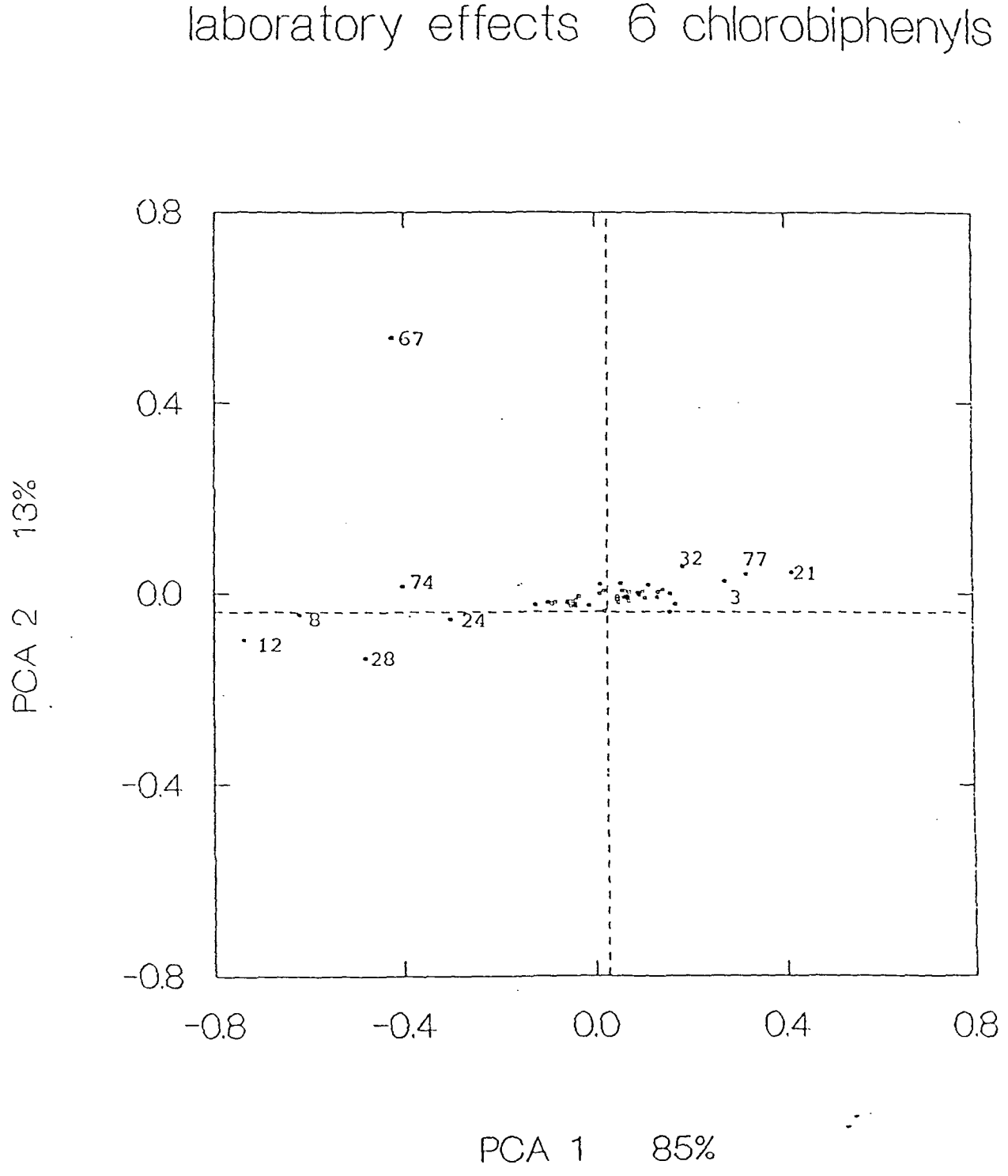

Figure 11 Principal component analysis. Percentage of total variance explained by both axes. The vertical ax is particularly correlated with CB-153, the horizontal ax is correlated with the CBs 101, 105, 138, 153, 180 and 189.

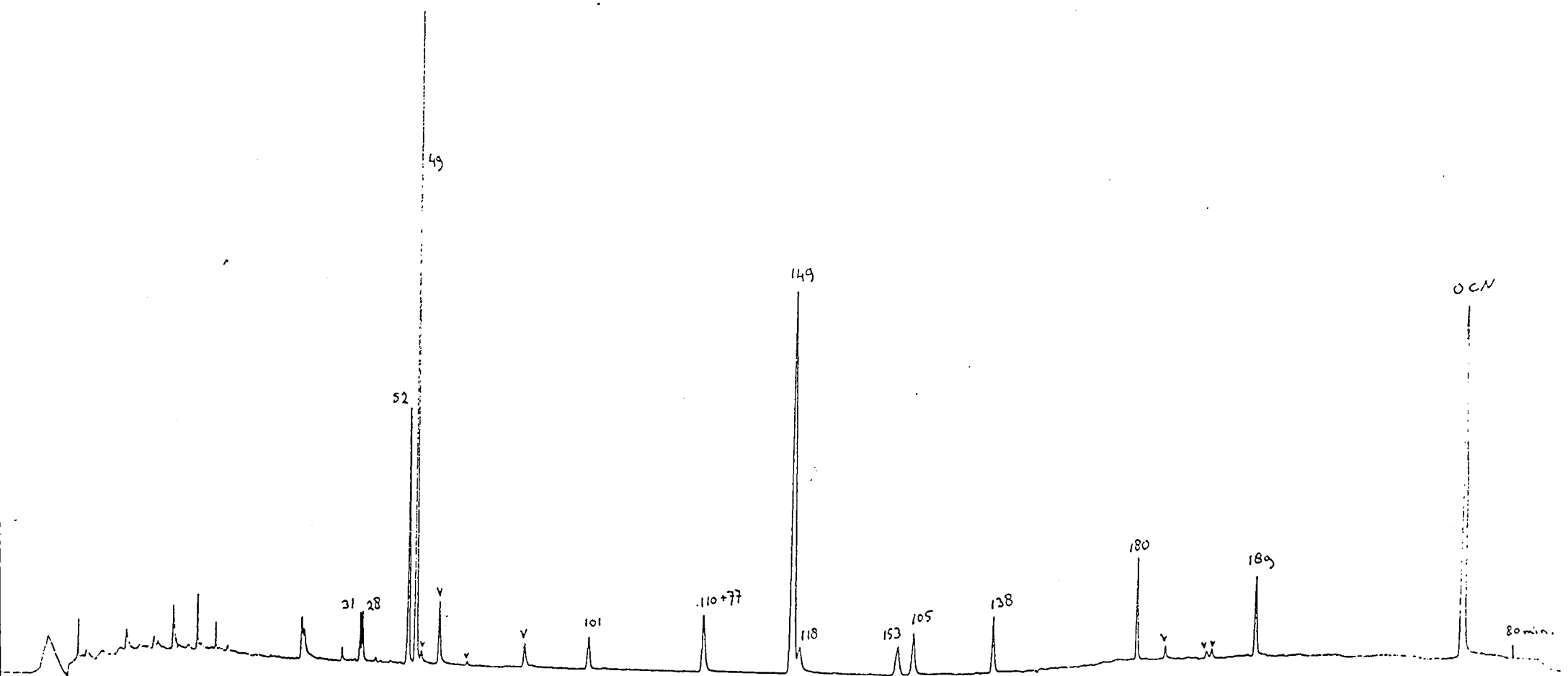

Figure 12 Chromatogram of the B solution (1/10 diluted) on a 50 m - 0.15 mm 5% phenyl - 95% methylpolysiloxane column.