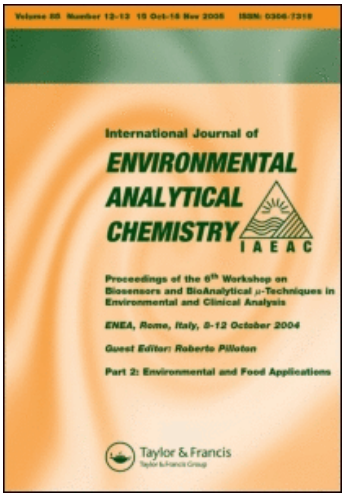

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DEVELOPMENT IN THE ANALYSIS OF CHLOROBIPHENYLS IN ENVIRONMENTAL MATRICES FOR CERTIFICATION PURPOSES

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The development of methods for the determination of chlorobiphenyls in environmental matrices for the certification of Reference Materials has recently concentrated on improving chromatographic separation techniques, chemical ionization-negative ion mass spectrometry, and the control of calibration procedures. The information has been disseminated through a BCR workshop, and the open literature. An overview of the progress made is given.

KEY WORDS: Chlorobiphenyls, capillary chromatography, reference materials, certification

INTRODUCTION

Chlorobiphenyls (CBs) have been analysed in environmental samples for some 30 years[1]. Initially they were determined on packed columns using industrial mixtures such as Aroclor 1254 to calibrate the gas chromatograph (GC)—electron capture detector (ECD), but with capillary columns, and in particular, fused silica columns in common use there has been a continual demand to measure more individual congeners[2].

The improvement in the separation of these congeners from each other has enabled researchers to determine more accurately those CBs which are toxicologically important and those which, because of their abundance, can be measured for monitoring purposes[3]. In recent years attention has focused on obtaining reliable analytical data[4,5] so that a more accurate assessment of the environmental impact of these contaminants can be made in different matrices covering each trophic level. The monitoring programmes[5,6] that have developed within and between institutes in member countries of the European Community require certified reference materials to validate the analytical methods and to maintain quality control as part of the validation of the environmental data.

In 1982 the Community Bureau of Reference (BCR) formed a working group for the analysis of chlorinated biphenyls and began a stepwise learning programme to

improve the quality of measurement[4]. This initial learning programme culminated in 1985 with the first of a series of certified reference materials (CRMs) for individual congeners in environmental matrices. These CRMs (Nos 349 and 350) were for seven CBs in cod liver and mackerel oil[8].

This paper reports on the co-operate studies undertaken by that BCR working group since 1985 and includes the developments in the separation and detection of individual CBs, the improvements in the quality of measurement made by this working group, and the programme for the certification of CBs in other environmental matrices.

WORKSHOP

The working group began in 1982 with thirteen laboratories drawn from member states of the EC, and in 1985 a three day workshop was devised to disseminate the information and experience gained by this group to other EC institutes who undertook similar analyses. The workshop was held at the State Institute for Quality Control and Agricultural Products (RIKILT) in The Netherlands in September 1987 to which twenty one institutes were invited, specifically including particularly the newer EC member states of Spain, Portugal and Greece.

The programme comprised of (i) an intercomparison exercise, which was completed in the participants own laboratory prior to the meeting, (ii) a series of discussions and seminars and (iii) a series of laboratory demonstrations with some "hands-on" exercises[5]. All participants were requested to analyse a sample of herring oil in triplicate, prior to the workshop, and to submit the data in preparation for a technical round table discussion. The herring oil supplied to the participants had previously been analysed by the original working group in 1985 as part of the initial learning programme. The data submitted was used to assess the analytical performance of the laboratories and to invite those who performed well to consider joining the BCR certification programme for CBs.

The herring oil was analysed for the seven "monitoring" CBs which had previously been selected by the BCR (Table 1) and the results from these laboratories are given in Table 2. These data are selected from those laboratories who were able to demonstrate that the analysis was under control. Data which clearly showed poor control or lack of correct calibration or optimization procedures within the laboratory were withdrawn at this stage. A number of laboratories were unable to undertake the analysis using capillary GC and some were unable to detect the presence of the CBs in the herring oil, either because the methods of clean-up were not used in the most efficient way or because the GC and some were unable to detect the presence of the CBs in the herring oil, either because the methods of clean-up were not used in the most efficient way or because the GC was not sufficiently optimized or calibrated. Those laboratories which did not possess a capillary column GC at the time used packed columns. The results of the workshop confirmed, for them, that it was necessary to have a capillary column chromatographic capability before proceeding further with this type of analysis. Other laboratories used the

Table 1 Chlorobiphenyls selected for the BCR certification programme

IUPAC No.	*Name*	*Formula*
Series 1 1982–1989		
28	2,4,4′ Trichlorobiphenyl	$C_{12}H_7Cl_3$
52	2,5,2′,5′ Tetrachlorobiphenyl	$C_{12}H_6Cl_4$
101	2,4,5,2′,4′ Pentachlorobiphenyl	$C_{12}H_5Cl_5$
118	2,4,5,3′,4′ Pentachlorobiphenyl	$C_{12}H_5Cl_5$
138	2,3,4,2′,4′,5′ Hexachlorobiphenyl	$C_{12}H_4Cl_6$
153	2,4,5,2′,4′,5′ Hexachlorobiphenyl	$C_{12}H_4Cl_6$
180	2,3,4,5,2′,4′,5′ Heptachlorobiphenyl	$C_{12}H_3Cl_7$
Series 2 (In addition to series 1)*		
105	2,3,4,3′,4′ Pentachlorobiphenyl	$C_{12}H_5Cl_5$
128	2,3,4,2′,3′,4′ Hexachlorobiphenyl	$C_{12}H_4Cl_6$
149	2,4,5,2′,3′,6′ Hexachlorobiphenyl	$C_{12}H_4Cl_6$
156	2,3,4,5,3′,4′ Hexachlorobiphenyl	$C_{12}H_4Cl_6$
170	2,3,4,5,2′,3′,4′ Heptachlorobiphenyl	$C_{12}H_3Cl_7$

* CB163 is also included to verify the separation from CB 138.

formulations as a basis for calibration and were only able to determine a "total" PCB value. Some laboratories were unable to obtain sufficient resolution between closely eluting pairs of CB such as CB28/31, CB149/118 and CB153/105, while other workers had a high variance possibly because they were not using an internal standard.

Overall, the results of the workshop intercomparison were encouraging. The data highlighted a number of laboratories who had benefited from the advances made in trace organic analysis, particularly in capillary GC-ECD. The exercise also identified those laboratories who found difficulty with chlorobiphenyl analysis and yet were submitting data to international monitoring programmes. While this workshop was of benefit to these workers it also demonstrated that there is a continuing need for this type of programme undertaken by the BCR on a much wider scale.

Table 2 Results of the analysis of the herring oil submitted to the BCR workshop on CBs, Rikilt, The Netherlands, September 1987.

CBs IUPAC No.	*MEAN ug kg*$^{-1}$	*SD*	*N*
28	27.2	12.3	16
52	62.8	21.3	15
101	92.3	13.1	13
118	132.6	28.1	14
138	148.8	14.7	14
153	172.8	35.2	18
180	51.3	16.2	17

As a result of this exercise the working group was expanded to include those institutes who had performed with an acceptable proficiency in the intercomparison and were able to commit to resources of the laboratory to the BCR certification programme.

SELECTION AND SEPARATION OF CBs

The original seven CBs (Table 1) were selected by the BCR for monitoring purposes on the following basis; (i) abundance of the CBs in a wide number of environmental matrices, (ii) representative of the level of chlorination and (iii) separation prior to detection by ECD. CB118 was also included at that stage because it is toxic, relatively resistant to metabolism and abundant in most matrices contaminated with CBs.

Following the initial selection of CBs in 1982 considerable effort has been given to detecting potential interferences relating to the measurement of these congeners by GC.

CB31 and 28

Relatively early in the programme it was confirmed that it was possible to separate CB31 and CB28 on a routine basis by using a 50 m column with 0.22 mm internal diameter and a film thickness of 0.2 μm or more. De Boer[9] has shown that the narrow column, 0.15 mm i.d. gives a much improved separation and the CB28/31 can be resolved even with a 25 m column of this i.d. However, the increased pressure required to maintain the optimum linear velocity of around 25 cm sec^{-1} for helium and 40 cm sec^{-1} for hydrogen does require more particular attention to the possibility of leaks, particularly at the front end of the column. Normally a column of this diameter is only used with a split/splitless injector, however it is also possible to use the 0.15 mm i.d. with an on-column system provided a de-activated or coated retention gap of i.d. >0.25 mm is attached between the injector and the column. The only other CB that has a retention time similar to these CBs on a 5% phenyl methyl silicone phase is CB50, which with a 2,4,6 chloro substitution pattern, is present at $<1\%$ of the total CB content of technical mixtures.

CB138 and CB163

Both CB138 (2,3,4,2′,4′,5′ hexachlorobiphenyl) and CB163 (2,3,5,6,3′,4′ hexachlorobiphenyl) have a similar retention time both on CP Sil 8 and CP Sil 19 phases[10]. Most earlier workers considered that CB163 was unlikely to exist to any extent in technical mixtures[11,12]. Close examination of most chromatograms would suggest that the peak was homogeneous when samples were chromatographed on either phase. However, Roos *et al*[13] experimented with two dimensional chromatography coupled to a chemical ionization-negative ion mass spectrometer and found that the CB138 peak was, in fact, not homogeneous, and suspected that the "impurity" was the co-eluting congener, CB163. Neither CB138 or CB163 are relatively toxic

Table 3 Additional analysis of CRMs for CBs (values ug kg^{-1} mass fraction)

MATRIX	*CB101 (a)*	*CB101 (b)*	*CB84 (b)*	*CB138 (c)*	*CB138*	*CB163 (d)*
CRM 349 Cod liver oil	372 ± 17	380	<2	765 ± 66	618	156
CRM 350 Mackerel oil	163 ± 9	179	<2	274 ± 60	209	70
CRM 392 Sewage sludge	132 ± 22	150	50	286 ± 40	231	53
CRM 420 Mineral oil	1450 ± 180	1470	610	1344 ± 117	1054	212

(a) Certified value (b) ref 18
(c) Indicative values (d) ref 14

congeners, however, without any separation there is likely to be an overestimate for CB138. It was not possible to confirm this at the time as this chlorobiphenyl was not available. Larsen and Reigo[13] synthesized CB163 and confirmed that this congener did occur in a number of environmental matrices. They managed to separate CB138 and CB163 on a 30 m very polar bis-cyanopropylphenyl phase, and confirmed that for some environmental compartments most estimates of CB138 using a simple non-polar phase is likely to produce an over-estimate of the true value by some 20–30% in some matrices (Table 3), if this type of column was not used.

However, the disadvantages are that these polar phases are not tolerant of the elevated temperatures necessary to elute higher boiling, less volatile, material which have been co-injected, particularly when using on-column injection. In addition, only a few of the retention times of the CBs are currently known for this phase. To date, the elution order of all of the 209 CBs are only known for the SE 54 (CP Sil 8) type column, based on the early studies by Mullins *et al*[10]. Fischer and Ballschmiter[15] have determined the retention times of 179 CBs on a 50% n-octyl methyl polysiloxane phase, which, apart from the study by Mullins, is the most complete set of retention data. Thus the CP Sil 88/SP2330 column may be used for confirmatory purposes, but some caution is still required if it is to be used for quantitation of CBs.

Recently, there have been some liquid chromatographic (LC) separations of different CB classes prior to GC. These have been based mainly on the substitution of the ortho-chloro position on the biphenyl rings[16]. It is now possible to effectively separate CB138 and CB163 using a pyrene bonded silica LC column and to determine these CBs in the two different eluates using the conventional 5% phenyl-methyl phases (e.g. CPSil 8 or SE 54) where the retention times of all CBs are known[17].

CB101, 84 and 90

De Boer[18] has reported that the determination of CB101 on a 5% phenyl methyl silicone phase might be affected in some environmental matrices by the presence of CB84 (2,3,6,2'3' pentachlorobiphenyl) and CB90 (2,3,5,2',4' pentachlorobiphenyl). This separation was studied using multi-dimensional GC (MDGC) by heart-cutting

the area around the CB101 and chromatographing the heart-cut on a SB-Smectic phase. The main advantage of this phase is that the retention of the CBs is a function of the planar nature of the rings, in similar way to the "pyrene LC" phase. However, the Smectic phase was initially designed to operate for supercritical fluid chromatography and, at present does have some drawbacks in it's application for GC. Hydrogen cannot be used as a carrier gas, it has a relatively high bleed and is not stable at elevated temperatures[19].

MDGC has been an extremely valuable tool in separating trace quantities of CB which elute very closely to the peak of interest. At present this technique only gives a semi-quantitative estimate since the method to heart cut the CBs along with the internal standard has still to be validated.

However, each of the CBs 101, 90 and 84 can be fully resolved on a more polar phase, CP Sil 19 which is the preferred column when more than one of these compounds are present in the matrix.

CB153, 105 and 132

Recently there has been a more widespread interest in the determination of the mono-ortho CB105 primarily because of its toxicological properties. It is possible to separate the CB153 from other congeners on a 5% methyl silicone (CPSil 8) phase, but it is more difficult to resolve the CB132 from CB105 which elutes immediately after the CB153. De Boer has demonstrated that it is possible to separate these by MDGC using a Smectic phase as the second column[20]. It is also possible to resolve the CB105 from CB132 prior to GC by passing the sample through a pyrene bonded column to separate the mono-ortho CB105 into another fraction[16,17]. The two different solutions can then be chromatographed on a GC capillary column where the retention times of all the CBs are known.

Choice of chromatographic columns

The initial choice of columns used for the determination of CBs was based on the methyl silicone (CPSil 5, OV 1 type) and the 5% phenyl methyl silicone (CPSil 8, SE54 type)[3]. The early discussions of the BCR working group on column selection identified that the simple methyl silicone phase was not sufficiently polar to separate key groups of CBs. The selection was modified to exclude the CPSil 5 type and to include the columns of similar polarity to CPSil 19 and OV17. These phases can separate six of the seven selected congeners from other co-eluting peaks provided that care is taken to optimize the GC. The only pair which require a higher polarity column is CB138 and CB163. These may be separated on a CPSil 88 type 100% cyanopropyl silicone phase. De Boer *et al*[20] have made a detailed study on the separation of 51 CBs on 7 different stationary phases in relation to the determination of these monitoring CBs.

In addition to the choice of stationary phase, it is equally essential to also select the most appropriate physical dimensions of the column. In general, it is difficult to obtain the necessary resolution with columns of i.d. of greater than 0.25 mm. Narrow

bore columns are essential for the maximum resolution of many of these closely eluting peaks. The separation is also enhanced by using a film thickness of between 0.2 and 0.5 um. Thinner films of 0.1 um have a slightly better resolution, but have a lower capacity, whilst thicker film columns of 0.5 um or more considerably increase the retention times. With these very thick films the maximum operating temperature of the column can be reached before the less volatile CBs have eluted, requiring the compound to be chromatographed during the isothermal period of the GC programme. The required separation between key CB pairs have only been achieved with a column length of 50 m or more, an i.d. of 0.25 mm or less and with a gas pressure adjusted to produce the most efficient mobile phase velocity. It is essential that the gas velocity is not increased to reduce the analysis time on the longer column as this will negate the whole purpose of the increased column length.

DETECTION AND CALIBRATION

The electron capture detector (ECD) is the workhorse for most routine determinations of organohalogen contaminants and for CBs in particular, and the mass spectrometer (MS) is often only used for confirmatory purposes when very accurate measurements are required. The conclusions from the BCR intercomparison exercises between 1982–85[3] were that the mass spectrometer, whilst giving additional specificity to the identification of the compounds eluting from the capillary column, tended to give a less precise measurement. This higher variance was primarily caused by the intrinsic designs of the system, and of the ion source in particular. Therefore data generated for certification purposes was restricted to the ECD. However, since the early '80s, there has been a considerable improvement in the design and capability of mass spectrometry. The negative ion-chemical ionization (NICI) MS capability has become a standard feature on most MS systems with a sensitivity which is as good as, if not better than, the ECD. The measurement made with the MS in the NICI mode is also considerably more precise than the MS data reported in the earlier intercomparison exercises. Although the differences between mass spectra of CBs are generally slight, making it difficult to distinguish between similar congeners, it is possible to examine the homogeneity of the eluting material[13] and confirm whether there is more than one compound present. This was particularly valuable in identifying CB163 as part of the CB138.

The experience in a recent certification programme to determine CBs in waste mineral oil demonstrated that NICI-MS has a similar sensitivity and precision as the ECD[21].

The effect of poor calibration procedures was evident in the initial series of the BCR intercomparison exercisees[3–5], and the first attempts to overcome this were based on measuring the most linear region and dynamic working range of the ECD, and then every effort was made to operate within the most linear part of the detector's response curve. However, this did mean that the minimum mass of compound was restricted to around 50 pg on column making it necessary to concentrate most sample extracts to increase the concentration above the minimum value. This approach is

only necessary if a single or two solutions which bracket the sample are used as calibrants.

When a multi-level calibration is made then it is possible to extend the range of the measurement fully to where the detector response is clearly non-linear without any reduction in accuracy[21]. The basic criteria is that the detector response per unit mass injected must not change between calibration points by more than 10%. If the change is greater than 10% then an additional intermediate calibration point must be added to the multi-level calibration.

CERTIFIED REFERENCE MATERIALS FOR CBs

The initial improvement in the quality of measurement of CBs previously reported for the fish oils by the BCR working group has been maintained for other matrices which have been analysed. In 1985 the group held an intercomparison to determine the level of CBs in a dried sewage sludge and after some discussion and further modifications to the methodologies the exercise was extended with a different set of samples to certify the sludge. A comparison of the coefficient of variation between the early data and that obtained during the certification programme is given in Figure 1. The reduction in variance from between 20–51% to below 18% demonstrates the improvement in the performance of the participants in these exercises. This group of participants comprised of some of the original members and those who joined the group in 1987 following the BCR CB Workshop.

The main recommendations which have been drawn from the workshop and subsequent studies are as follows:

- Capillary column chromatography is essential for the separation and determination of CBs.
- Total measurement of PCBs based on formulations as calibrants is not appropriate under any circumstances.
- Pure single congeners should always be used as calibrants.
- The quality of the calibration solutions must be carefully verified.
- The calibration of the ECD should match the response curve over the working range to within $\pm 10\%$.
- Correct selection of the stationary phase, and column dimensions are essential.

  Column length should be a minimum of 50 m.
  Column i.d. not greater than 0.25 mm.
- Optimization of the chromatographic separation of the CBs.
- The thoroughness of clean-up to reduce unwanted interference from co-extracted materials.

The BCR now has certified the CB content of four matrices (Table 4) and the coefficient of variation of each of the congeners plotted against the mean value obtained in the certification exercise is given in Figure 2. The CV% for all the

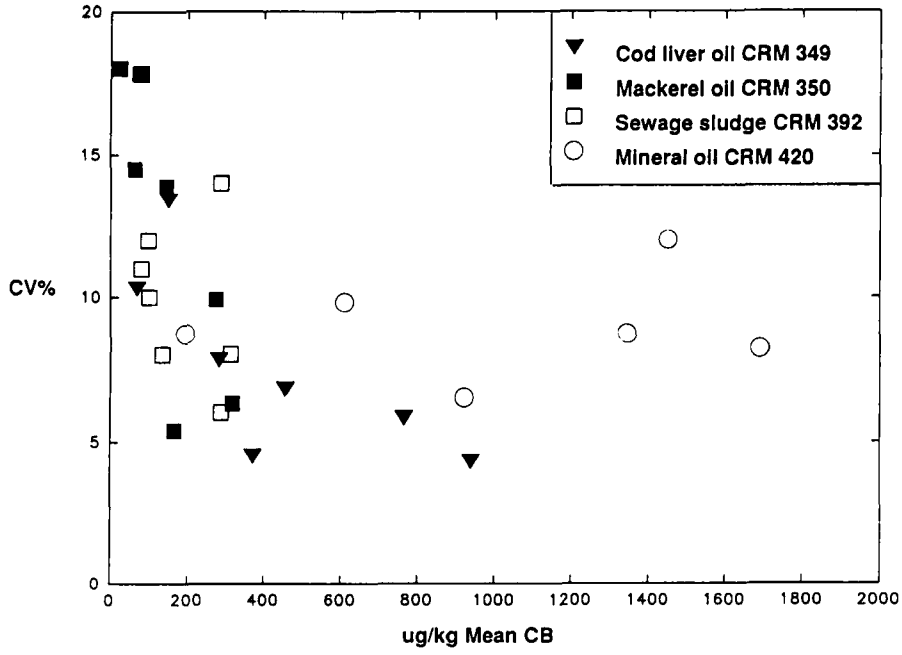

Figure 1 Coefficient of variation (CV) vs the interlaboratory mean values for the seven CBs in certified RMs.

determinand are below 20% and some are as low as 5%. As well as the development of a valuable series of certified RMs these data also confirm that it is now possible to consistently make reliable measurements of CBs and obtain agreement between groups of 15–20 laboratories within the European Community. This level of agreement is not something peculiar to this group, but only represents what is possible with commitment and the available technology and operating procedures.

Currently, the BCR CB programme includes the measurement of 12 congeners (Table 1) in a second mineral oil which has been spiked at a high level (ca

Table 4 BCR certified reference materials CBs in environmental matrices

CRM	*Certified congeners*	*Congeners with indicative values*
Cod liver oil		
CRM 349	28, 52, 101, 118, 152, 180	138 + 163
Mackerel oil		
CRM 350	28, 52, 101, 118, 153, 180	138 + 163
Dried sewage sludge		
CRM 393	28, 52, 101, 118, 153, 180	138 + 163
Waste mineral oil (low level)		
CRM 420	28, 101, 118, 153, 180	138 + 163

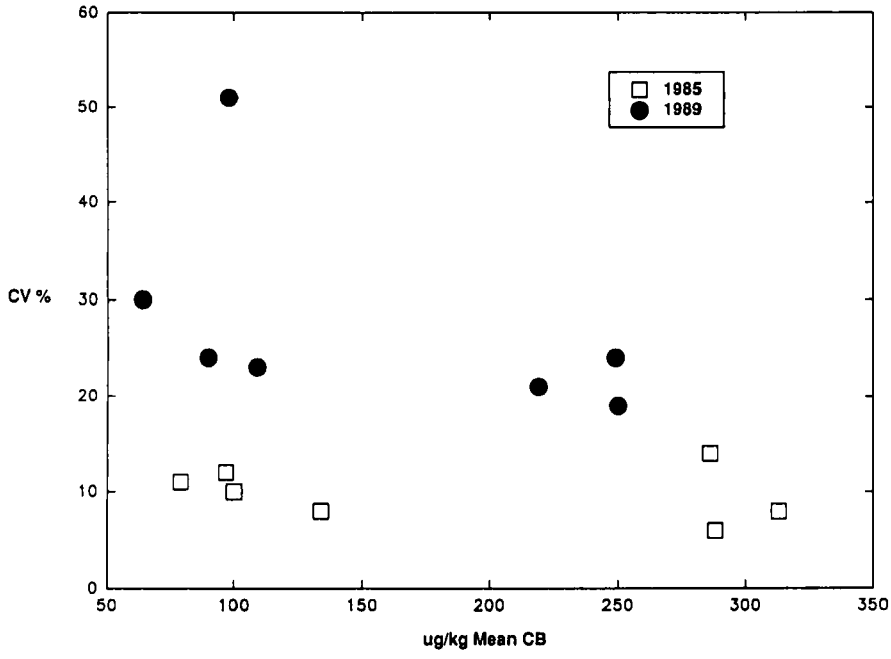

Figure 2 Coefficient of variation (CV) vs the laboratory mean values for the seven CBs in sewage sludge showing the improvement between laboratories from 1985 to 1989.

200 mg kg^{-1}) to represent the type of waste oil which is being illegally doped and dumped. The same congeners are being determined in a dried milk powder.

The profile of the CBs in the fish oils and the dried sewage sludge were similar to that found in the more common industrial mixtures such as Aroclor 1254. However, the level and distribution of CBs in mammalian tissue/fluids reflects effect of the normal metabolic activity. Most of the tri and tetra chlorobiphenyls are de-hydrochlorinated and/or hydroxylated to form soluble metabolites which are excreted. The four additional CBs, CB105, 128, 156 and 170 have been included in the certification programme, partially a replacement for CB28 and 52, which will only be present at the ultra trace level, and also to include other CB which are known to be toxicologically active. CB149 has also been added as a control over the separation of CB149 and CB118.

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