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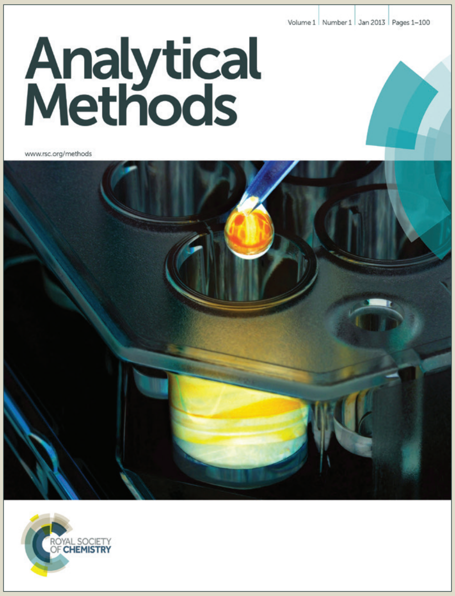

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COMPARISON OF DIFFERENT MASS SPECTROMETRIC TECHNIQUES FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS BY ISOTOPE DILUTION USING ^{37}Cl-LABELLED ANALOGUES

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ABSTRACT

This work presents the comparison of four different mass spectrometric techniques coupled to Gas Chromatography (single quadrupole ICP-MS, triple quadrupole ICP-MS/MS, single quadrupole NCI-MS and triple quadrupole EI-MS/MS) for the detection of Polychlorinated biphenyls (PCBs) in environmental samples and their determination by a new Isotope Dilution Mass Spectrometry (IDMS) approach. A mixture of twelve priority PCBs labelled with ^{37}Cl was employed as species-specific isotopically labelled internal standard. The ^{37}Cl-labelled PCBs enable the use of both molecular and elemental ionization sources, such as ICP or NCI, as the isotopic label is in the heteroatom. First, the comparison was carried out by assessing the capabilities of all instruments to measure chlorine isotope ratios and calculating the isotopic enrichment of the labelled analogues. Finally, the analysis of the Certified Reference Material SRM 1941b (organics in marine sediment) containing PCBs at the low ng g^{-1} range was carried out for method comparison. Elemental ionization sources such as ICP and NCI combined with quadrupole mass spectrometry provided chlorine specific detection and

high sensitivity for the higher chlorinated compounds but suffered from high background signals from other chlorine containing, co-eluting compounds in the sample which prevented the accurate measurement of the PCB-specific chlorine isotope ratios. On the other hand, the use of GC-MS/MS in the Selected Reaction Monitoring mode (SRM) provided selective and accurate measurements but suffered from lower sensitivity for the higher chlorinated compounds.

INTRODUCTION

PCBs are a group of 209 structurally related chemical compounds (congeners) that constitute a class of ubiquitous pollutants with aromatic structure, high chemical stability and extremely poor water solubility.[1] Although their manufacture has stopped already in 1977,[2] these toxic compounds are distributed at a global scale through atmospheric transport and can be found in almost every environmental compartment including air, water, sediments, fish and mammals as well as in every region of the world.[3-4] For these reasons, the development of reliable methods for PCBs determination in environmental samples is still highly important.[5]

PCBs have been mainly determined in real samples using Gas chromatography (GC) coupled to electron capture detection (ECD) or mass spectrometry (MS).[6] GC coupled to ECD or Negative Chemical Ionization (NCI-MS) provides high sensitivity but suffer from a lack of selectivity as all chlorinated compounds present in the sample matrix are detected.[7-9] In contrast, the use of electron ionization (EI) coupled to MS using the Selective Ion Monitoring mode (SIM) increases selectivity as only analyte-specific molecular fragments are detected. GC coupled to tandem mass spectrometry (GC-

MS/MS) with EI using Selected Reaction Monitoring (SRM) mode enhances even more the selectivity of PCBs determination compared to SIM.[10]

The coupling of GC to Inductively Coupled Plasma Mass Spectrometer (ICP-MS) has been established as powerful hyphenated technique in trace element speciation analysis,[11] particularly for the determination of volatile organometallic contaminants based on the element-specific determination of the heteroatom present in the molecule.[12] However, the determination of relevant halogenated contaminants by GC-ICP-MS is very limited[13-17] due to the high ionisation potential of halogen atoms, their low ionization efficiency in an argon plasma as well as different strong polyatomic interferences formed inside the plasma. For these reasons, GC-ICP-MS has never been applied to the determination of PCBs. Indeed, the only publication that can be found in the literature dealing with the determination of PCBs by ICP-MS is based on the use of electrothermal vaporization with the aim of differenciating "organic" chlorine and inorganic chlorine.[18] The use of ICP-MS instruments equipped with collision cells has been demonstrated to be an efficient approach to remove spectral interferences and decrease the detection limits of phosphorus, sulphur, bromine and chlorine or iodine containing compounds when analysed by GC-ICP-MS.[13] The recent commercialisation of triple quadrupole systems with the ICP source (ICP-QqQ) allows the improved resolution of problematic spectral interferences[19-20] when operated in MS/MS mode but it has not been evaluated as a GC detector thus far.

Isotope Dilution Mass spectrometry (IDMS) provides accurate and precise determinations directly traceable to the International System of units.[21] The determination of PCBs by IDMS has been traditionally carried out using multiply ^{13}C labelled analogues and methodological calibration graphs where the labelled analogues are employed as internal standards.[22] We have recently presented the synthesis of ^{37}Cl-

labelled PCBs and their application to the IDMS determination of PCBs in solid samples by GC-EI-MS/MS.[23] The use of ^{37}Cl-labelled analogues has been shown to provide analytical figures of merit comparable to those obtained using ^{13}C-labelled compounds as internal standards. On the other hand, the use of ^{37}Cl-labelled compounds allows for the selection of alternative ionization sources, both elemental and molecular. We present here for the first time the comparison of three different ionization sources (EI, NCI and ICP) and four different MS techniques (GC-MS, GC-MS/MS, GC-ICP-MS and GC-ICP-MS/MS) for the detection of PCBs in solid samples and the determination of selected PCBs by IDMS using their ^{37}Cl-labelled analogues. For this purpose, we carried out the evaluation of the different ion sources and mass spectrometer configurations for the characterization of a set of twelve ^{37}Cl-labelled congeners in terms of isotopic measurements. Finally, the analysis of the certified reference material SRM 1941b (marine sediment) was performed to evaluate the capabilities of the different mass spectrometric techniques for the accurate determination of selected PCBs at the low ng g^{-1} levels in real samples by IDMS.

EXPERIMENTAL SECTION

Reagents and Materials. A 10 µg g^{-1} solution of twelve PCBs (congeners 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 180, 194) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The ^{37}Cl-labelled PCBs mixture was synthesised in our laboratory as reported elsewhere.[23] Working standard solutions of labelled and unlabelled PCBs were prepared in isooctane (Sigma-Aldrich) and stored in the dark at 4°C until use. Hexane and acetone were obtained from (Sigma-Aldrich). Florisil was obtained from Supelco (Bellefonte, PA, USA). PTFE-coated magnetic stirring bars and 10 mL glass vessels employed for the microwave extractions were purchased from CEM Corporation

(Matthews, NC, USA). Cu powder was purchased from Merck (Darmstadt, Germany). The standard reference material SRM 1941b (organics in marine sediment) was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, USA).

Instrumentation.

Gas Chromatography was coupled in this work to four different mass spectrometric techniques. A single quadrupole Agilent 7700 (Agilent Technologies, Tokyo, Japan) was coupled to a GC model 6890 (Agilent Technologies, Waldbronn, Germany) equipped with a cold on-column injector and a DB-5MS column (15m × 0.25 mm i.d. × 0.1 µm film thickness) from Agilent (Santa Clara, USA). The same gas chromatograph was also coupled to an Agilent 8800 triple quadrupole ICP-MS (Agilent Technologies). A single quadrupole GC-MS model QP2010 Plus (Shimadzu, Kyoto, Japan) equipped with a NCI source, a split/splitless injector and a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) was also employed. Finally a gas chromatograph model Agilent 7890A (Agilent Technologies) fitted with a split/splitless injector and a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) was coupled to an Agilent 7000 triple quadrupole Mass Spectrometer equipped with an EI source. Operating conditions of all mass spectrometric techniques are summarized in Tables S1, S2 and S3 of the Electronic Supporting Information. The extraction of the PCBs from the solid sample was carried out by a focused microwave Explorer-12-Hybrid system (CEM Corporation). The centrifugation of the samples was performed using a centrifuge model CENTRO-8 BL (JP Selecta, Barcelona, Spain). An analytical balance model AB204-S (Mettler Toledo, Zurich, Switzerland) was used for the gravimetric preparation of all solutions and standards, while a mini-vap evaporator/concentrator

(Supelco, St. Louis, MO, USA) was used for the evaporation of the sample extracts to their final volume before injection.

Procedures.

Sample preparation for PCBs determination in the marine sediment SRM 1941b. The sample preparation procedure has been already described in a previous publication.[23] Briefly, the extraction of PCBs from the solid samples was carried out by focused microwave assisted extraction. Weighed amounts of sample and spike (approximately 0.1 g of sample and 0.1 g of a 7 ng g^{-1} solution of the isotopically labelled PCBs mixture) were added directly to a disposable 10 mL glass vial in which the focused microwave assisted extraction is carried out. The extraction solvent employed for the analysis of the marine sediment SRM 1941b was a 1:1 mixture of hexane and acetone. After microwave irradiation the extracts were centrifuged at 3000 rpm for 5 minutes. Then, 0.3 g of Cu powder was added to remove residual sulphur which is present in the sample. To assist the sulphur removal the sample was sonicated for 30 min. In addition, all the extracts were cleaned with a florisil column. Finally the extracts were preconcentrated with a gentle nitrogen flow until a volume of approximately 50 µL. Please note that the accurate knowledge of the final volume is not required by IDMS.

Measurement of the isotopic composition of the samples by the different mass spectrometric techniques. When using elemental ion sources such as ICP or NCI with a single quadrupole mass analyser, the elemental chlorine isotope ratio $^{37}Cl/^{35}Cl$ was measured. For the ICP measurements in the single quadrupole instrument He was employed as collision gas to remove the spectral interference $^{36}Ar^{1}H$ on ^{37}Cl. When the samples were measured by triple quadrupole ICP-MS/MS, hydrogen was used as reaction gas. Therefore, chlorine isotope ratios were measured as the ratio of $^{37}ClH_2$

(m/z 39) and $^{35}ClH_2$ (m/z 37). When using the GC-MS/MS system with an EI source, the SRM transitions for the natural abundance and ^{37}Cl-labelled PCBs as well as the collision energies employed for collision induced dissociation (CID) were those reported elsewhere.[23]

Target PCB congeners. A set of twelve PCB congeners was selected to carry out the comparison of the different MS techniques. This set included the six non-dioxin-like PCBs congeners 28, 52, 101, 138, 153 and 180 that are considered as indicators by the EFSA (European Food Safety Authority), the 'dioxin-like' congener PCB 118, to which a toxic equivalency factor has been assigned by the World Health Organization, and five other congeners relevant due to their widespread presence in the environment (18, 31, 44, 149 and 194). This group of congeners is listed in the International Standard IEC 61619-1997 for the determination of PCBs by capillary GC in insulating liquids.

RESULTS AND DISCUSSION

Measurement of elemental chlorine isotope ratios by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS.

First, the precision and accuracy of the measurement of the compound-specific chlorine isotope ratios $^{37}Cl/^{35}Cl$ were evaluated by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS. For this purpose, five independent injections of a mixture of the natural abundance PCBs were carried out with each technique. The concentration of the natural abundance standard employed was 200 ng g^{-1} when using the ICP-MS instruments whereas three different concentration levels (100, 500 and 1000 ng g^{-1}) were tested when using the NCI source. Detector dead time was corrected in all measurements and the final results obtained are given in Table 1. A significant mass discrimination effect was observed when using the GC-ICP-MS and GC-ICP-MS/MS instruments. When comparing the experimental values with the theoretical $^{37}Cl/^{35}Cl$ isotope ratio, the relative error varied from 0.6% to 11.2% by GC-ICP-MS and from 2.8% to 11.9% by GC-ICP-MS/MS, respectively. The precision obtained calculated as Relative Standard Deviation (RSD%) from three GC injections ranged from 2.3% to 11.2% by GC-ICP-MS and from 2.7% to 10% by GC-ICP-MS/MS. A much better accuracy and precision was obtained when using the GC-NCI-MS system. The relative error obtained in the isotope ratio for all congeners ranged from 0.01% to 2.6% while the RSD values ranged from 0.1% to 0.7%. In addition, we did not observed any difference in the measured isotope ratios at the three levels of concentration tested, indicating that an adequate detector dead time correction was applied and the absence of other detector effects within the concentration range tested.

Determination of the isotope enrichment of ^{37}Cl-labelled PCBs.

The isotopic enrichment of ^{37}Cl in the different ^{37}Cl-labelled PCB congeners contained in the spike solution employed in this work was calculated on the basis of the results obtained by all the different techniques. The values obtained by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS were directly calculated from the detector dead time and mass bias corrected measurement of the compound-specific $^{37}Cl/^{35}Cl$ isotope ratio. Mass bias was corrected by external bracketing injecting a natural abundance standard containing the twelve target PCBs congeners every three samples. The isotopic enrichments obtained by GC-EI-MS/MS[23] were calculated as described elsewhere.[24] Briefly, the isotope distribution of each congener is compared with theoretically derived spectra calculated for different tentative isotope enrichments. The best isotope enrichment was that which provided the minimum in the square sum of residuals for the linear regression between the theoretical and experimental spectra. In all cases the uncertainty of the values corresponds to the standard deviation of *n=5* independent GC injections. The results obtained are given in Table 2. As can be seen, most of the isotopic enrichments obtained agree well between all techniques. We only found significant differences when comparing the values obtained by GC-NCI-MS and GC-EI-MS/MS in four congeners, mainly due to low standard deviation of the values in comparison with those obtained using GC-ICP-MS and GC-ICP-MS/MS.

Determination of the ^{37}Cl-labelled PCBs concentration by reverse IDMS.

The concentration of the ^{37}Cl-labelled PCBs contained in the spike solution employed in this work was carried out by reverse IDMS. For each of the instruments tested, three independent blends of the spike solution and a natural abundance standard containing all target congeners were prepared and injected each in triplicate. The concentrations obtained by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS were calculated applying the classical IDMS equation using the compound specific ^{37}Cl/^{35}Cl isotope ratio. The concentrations obtained by GC-EI-MS/MS were calculated by multiple linear regression as described elsewhere.[23] Figure 1 shows the comparison of the results obtained with the four techniques. As can be observed, significant differences between the different MS techniques were obtained for all congeners. As there are no reference values for this spike solution we cannot discuss on the accuracy of the different measurements. Therefore, technique-specific concentrations of the labelled PCBs were employed for the subsequent analysis of the certified reference material 1941b.

Analysis of the certified reference material SRM 1941b (marine sediment).

We have previously demonstrated[23] that the use of a 1:1 mixture of hexane and acetone and a focused microwave assisted extraction at 70ºC for 4 minutes provided quantitative recoveries for all target congeners present in the certified sediment SRM 1944 in a concentration range from 11 to 80 ng g^{-1}. Therefore the same sample preparation procedure was employed here for the analysis of the sediment SRM 1941b. However, it is important to highlight that the concentration level of the target PCB congeners in this material ranged from 1 to 8 ng g^{-1}. It is also important to note that, besides the twelve target PCBs, this material provides also certified values for 30 additional PCB congeners as well as 7 chlorinated pesticides.

When using the GC-ICP-MS system (single quadrupole) helium was employed as collision gas to remove spectral interferences. However, preliminary analyses of this material showed that the sensitivity obtained was not enough to perform a reliable quantification of the target PCBs at the SRM 1941b concentration range. In addition to the low sensitivity, the coelution of other chlorinated compounds prevented integration of most target congeners. Therefore, we could not provide concentration values for this material using GC-ICP-MS. It is worth stressing that the use of a 30m column instead of a 15 m column might significantly improve the chromatographic resolution.

Figure 2 shows the comparison of the certified values with the experimental values obtained in the analysis of SRM 1941b using GC-ICP-MS/MS, GC-NCI-MS and GC-EI-MS/MS. For GC-ICP-MS/MS analyses, H_2 was employed as reaction gas to remove spectral interferences through the formation of ^{37}Cl-H_2 (m/z 39) and ^{35}Cl-H_2 (m/z 37).

Figure 3 shows a GC-ICP-MS/MS chromatogram of the SRM 1941b spiked with the mixture of ^{37}Cl-labelled PCBs. The chromatogram for transition $^{35}\mathrm{Cl} \rightarrow {}^{35}\mathrm{Cl}$-$\mathrm{H}_2$ shows that the signal to noise ratio is not satisfactory and that the presence of other chlorinated compounds hampers the proper integration of many of the target congeners. In contrast, the chromatogram for the transition $^{37}\mathrm{Cl} \rightarrow {}^{37}\mathrm{Cl}$-$\mathrm{H}_2$ shows a much better signal to noise ratio. Under these conditions, we could only determine experimental concentrations for PCB 28+31, 101, 180 and 194 and, as can be observed in Figure 2, they were in good agreement with the certified values. However, the RSD values obtained from three independent extractions ranged from 9 to 57%. Here the further improvement of the chromatographic separation conditions in term of resolution (e.g. using a 30m column length) might help to minimize possible coelution and therefore will improve the integration of the targeted compounds.

Figure 4 shows that the GC-NCI-MS system provides, among all the evaluated techniques, the highest sensitivity for PCBs determination in SRM 1941b. However, the presence of other chlorinated compounds and an important background at m/z 35, hampered the proper integration of several congeners such as 138, 153 and 149. The results obtained using this technique for the rest of congeners are also shown in Figure 2. As can be seen, we could not provide any concentration in agreement with the certified values of the material probably due to the high background at m/z 35. The RSD values obtained from three independent extractions ranged from 4 to 27%.

Finally, Figure 5 shows that the GC-EI-MS/MS system provided the best signal to noise ratio and a very low background both for the natural abundance and for the labelled analogues at the selected transitions. Using this technique, sequential detection windows based on the elution time and the PCB chlorination degree are programmed. In this way the only interference that may affect the analyte peak can only be due to a PCB congener with the same chlorination degree. As can be observed in Figure 5, GC-EI-MS/MS allowed the accurate integration of all target congeners except for PCB 18, 153 and 138. Also, the concentration of PCB 194 was too low to provide an accurate integration. It is worth noting that none of the MS techniques employed in this work allowed us to obtain concentration values for PCB 153 and 138, indicating that the quantification problem for these congeners is due to an incomplete chromatographic separation rather than an instrumental limitation. Figure 2 shows that GC-EI-MS/MS provided concentrations in good agreement with the certified values for the rest of the target PCBs with a precision ranging from 1.6 to 8.1% (RSD).

CONCLUSIONS

Using ^{37}Cl-labelled PCBs it is possible to employ different ionization sources and mass analyzers to determine PCBs by IDMS. In this way, it is possible to compare the capabilities of different ion sources and mass analyzers coupled to GC. This work has shown that GC-EI-MS/MS is the technique that provides more accurate and precise results in the analysis of real samples as the SRM mode provides the most specific detection for each PCB congener. A higher instrumental sensitivity is obtained when using GC-NCI-MS, but the interferences due to the presence of other co-eluting chlorinated compounds and the high background at m/z 35 prevented its application to real samples at low concentration levels. Nevertheless, it is worth commenting that accurate and precise compound specific isotope ratios were obtained by GC-NCI-MS. Finally, according to our results, the use of GC-ICP-MS and GC-ICP-MS/MS for the determination of PCBs offers no advantages over the more traditional GC-EI-MS/MS technique. Although we could obtain experimental concentrations in agreement with the certified values for 5 congeners in the analysis of SRM 1941b, the signal to noise ratio and the precision of the results was poor in comparison with GC-EI-MS/MS. In addition, the precision obtained in the measurement of compound-specific chlorine isotope ratio in standards was not satisfactory, in comparison with that obtained by GC-NCI-MS. Here further instrumental improvements and optimizations might help to enhance the sensitivity and to further reduce the present interferences. Also the optimization of the chromatographic conditions with respect to improve the resolution and therefore the separation between targeted PCBs and co eluting as well as co extracted chlorinated compounds will help to improve the performance of the different setups in the future.

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REFERENCES

[1] B.D. Rodan, D.W. Pennington, N. Eckley and R. Boethling, *Environ. Sci. Technol.,* 1999, **33**, 3482.

[2] K.J. Kelly, E. Connelly, G.A. Reinhold, M. Byrne and D.J. Prezant, *Arch. Environ. Health,* 2002, **57**, 282.

[3] A. Beyer and M. Biziuk, *Rev. Environ. Contam. Toxicol.,* 2009, **201**, 137.

[4] K. Jaraczewska, J. Lulek, A. Covaci, S. Voorspoels, A. Kaluba-Skotarczak, K. Drews and P. Schepens, *Sci. Total Environ.,* 2006, **372** ,20.

[5] H.P. Tang, *TRAC-Trend. Anal. Chem.,* 2013, **45**, 48.

[6] S.P.J. van Leeuwen and J. de Boer. *J. Chromatogr. A.,* 2008, **1186**, 161.

[7] C. Danielsson, K. Wiberg, P. Korytár, S. Bergek, U.A.T. Brinkman and P. Haglund, *J. Chromatogr. A.*, 2005, **1086**, 61.

[8] M. Ramil-Criado, D. Hernanz-Fernández, I. Rodríguez-Pereiro and R. Cela-Torrijos, *J. Chrom. A.,* 2004, **1056**, 187.

[9] H. Kontsas and K. Pekari, *J. Chromatogr. B.,* 2003, **791**, 117.

[10] P. Plaza Bolaños, A. Garrido Frenich, and J.L. Martinez Vidal, *J. Chromatogr. A.,* 2007, **1167**, 9.

[11] M. Popp, S. Hann and G. Koellensperger, *Anal. Chim. Acta*, 2010, **668**, 114.

[12] Bouyssiere, J. Szpunar and R. Lobinski*, Spectrochim. Acta Part B,* 2002*,* **57***,* 805.

[13] D. Pröfrock, P. Leonhard, S. Wilbur and A. Prange, *J. Anal. At. Spectrom.*, 2004, **19**, 623.

[14] N. Fidalgo-Used, M. Montes-Bayon, E. Blanco-Gonzalez and A. Sanz-Medel. *Talanta*, 2008, **75**, 710.

[15] A. Gonzalez-Gago, J. M. Marchante-Gayon and J. I. Garcıa Alonso, *J. Anal. At. Spectrom.*, 2007, **22**, 1138.

[16] J. L. Gomez-Ariza, T. Garcıa-Barrera and F. Lorenzo, *J. Anal. At . Spectrom.*, 2005, **20**, 883.

[17] J. L. Gomez-Ariza and T. Garcıa-Barrera, *J. Anal. At. Spectrom*., 2006, **21**, 884.

[18] Richner and S. Wunderli, *J. Anal. At. Spectrom.,* 1993, **8**, 45.

[19] S. Diez Fernández, N. Sugishama, J. Ruiz Encinar and A. Sanz-Medel, *Anal. Chem*., 2012, **84**, 5851.

[20] L. Balcaen, G. Woods, M. Resano and F. Vanhaecke, *J. Anal. At. Spectrom*., 2013, **28**, 33.

[21] J.I. García Alonso and P. Rodríguez González in *Isotope Dilution Mass Spectrometry*, Royal Society of Chemistry, Cambridge, 2013.

[22] T. Otake, Y. Aoyagi, T. Yarita and M. Numata, *Anal. Bioanal. Chem.*, 2010, **397**, 2569.

[23] L. Somoano Blanco, P. Rodriguez-Gonzalez, S. García Fonseca, J.I. Garcia Alonso, *Anal. Chem.*, in press.

[24] A. González-Antuña, P. Rodríguez-González and J. I. García Alonso, *J. Mass Spectrom.*, 2014, **49**, 681.

Table 1. Compound-specific $^{37}Cl/^{35}Cl$ isotope ratios measured by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS in a standard mixture containing twelve natural abundance PCB congeners. Uncertainty of the values corresponds to the standard deviation of n=5 injections. The theoretical value of the $^{37}Cl/^{35}Cl$ isotope ratio was established as 0.3200. Results with GC-NCI-MS are given at three different concentration levels (100, 500 and 1000 ng g^{-1}).

PCBs Congeners	**GC-ICP-MS 200 ng g^{-1}**	**GC-ICP-MS/MS 200 ng g^{-1}**	**GC-NCI-MS 100 ng g^{-1}**	**GC-NCI-MS 500 ng g^{-1}**	**GC-NCI-MS 1000 ng g^{-1}**
PCB-18	0.343 ± 0.014	0.329 ± 0.020	0.3229 ± 0.0012	0.3236 ± 0.0015	0.3283 ± 0.0016
PCB-28+31	0.337 ± 0.012	0.345 ± 0.015	0.3246 ± 0.0005	0.3191 ± 0.0017	0.3222 ± 0.0021
PCB-52	0.341 ± 0.011	0.356 ± 0.036	0.3235 ± 0.0002	0.3222 ± 0.0015	0.3265 ± 0.0016
PCB-44	0.322 ± 0.009	0.331 ± 0.018	0.3227 ± 0.0007	0.3208 ± 0.0017	0.3248 ± 0.0016
PCB-101	0.330 ± 0.028	0.348 ± 0.026	0.3241 ± 0.0004	0.3222 ± 0.0016	0.3262 ± 0.0017
PCB-118	0.349 ± 0.010	0.358 ± 0.025	0.3229 ± 0.0002	0.3208 ± 0.0017	0.3250 ± 0.0018
PCB-149	0.317 ± 0.036	0.349 ± 0.020	0.3253 ± 0.0003	0.3236 ± 0.0017	0.3276 ± 0.0016
PCB-153	0.338 ± 0.013	0.342 ± 0.014	0.3237 ± 0.0004	0.3220 ± 0.0018	0.3266 ± 0.0016
PCB-138	0.350 ± 0.008	0.349 ± 0.014	0.3234 ± 0.0003	0.3202 ± 0.0018	0.3249 ± 0.0020
PCB-180	0.359 ± 0.023	0.356 ± 0.010	0.3238 ± 0.0008	0.3216 ± 0.0019	0.3266 ± 0.0017
PCB-194	0.341 ± 0.013	0.352 ± 0.018	0.3236 ± 0.0006	0.3222 ± 0.0015	0.3272 ± 0.0016

Table 2. Isotopic enrichment (at% of ^{37}Cl) for the different ^{37}Cl-labelled PCB congeners. The values obtained by GC-ICP-MS, GC-ICP-MS/MS and GC-NCI-MS were calculated from the measurement of the ^{37}Cl/^{35}Cl isotope ratio whereas the values calculated by GC-EI-MS/MS were calculated as described elsewhere.[24] Uncertainty of the values corresponds to the standard deviation of n=5 independent GC injections.

PCBs Congeners	GC-ICP-MS	GC-ICP-MS/MS	GC-NCI-MS	GC-EI-MS/MS[23]
PCB-18	93.98 ± 0.68	93.50 ± 0.43	94.30 ± 0.11	94.14 ± 0.06
PCB-28+31	94.06 ± 0.23	93.65 ± 0.41	93.83 ± 0.09	94.05 ± 0.04
PCB-52	94.25 ± 0.25	94.59 ± 0.51	94.42 ± 0.02	94.16 ± 0.03
PCB-44	94.38 ± 0.56	93.78 ± 1.99	94.36 ± 0.06	94.06 ± 0.03
PCB-101	94.48 ± 0.23	94.16 ± 1.76	94.13 ± 0.30	94.06 ± 0.06
PCB-118	94.21 ± 0.74	92.93 ± 1.81	93.93 ± 0.12	93.99 ± 0.03
PCB-149	92.27 ± 0.61	91.95 ± 0.66	92.49 ± 0.07	92.51 ± 0.02
PCB-153	93.57 ± 0.84	92.00 ± 1.64	92.70 ± 0.29	92.70 ± 0.03
PCB-138	93.56 ± 0.38	92.54 ± 1.13	92.71 ± 0.04	92.70 ± 0.03
PCB-180	92.13 ± 0.47	91.59 ± 0.67	91.91 ± 0.06	91.93 ± 0.03
PCB-194	91.25 ± 0.46	91.34 ± 0.60	91.65 ± 0.08	91.45 ± 0.03

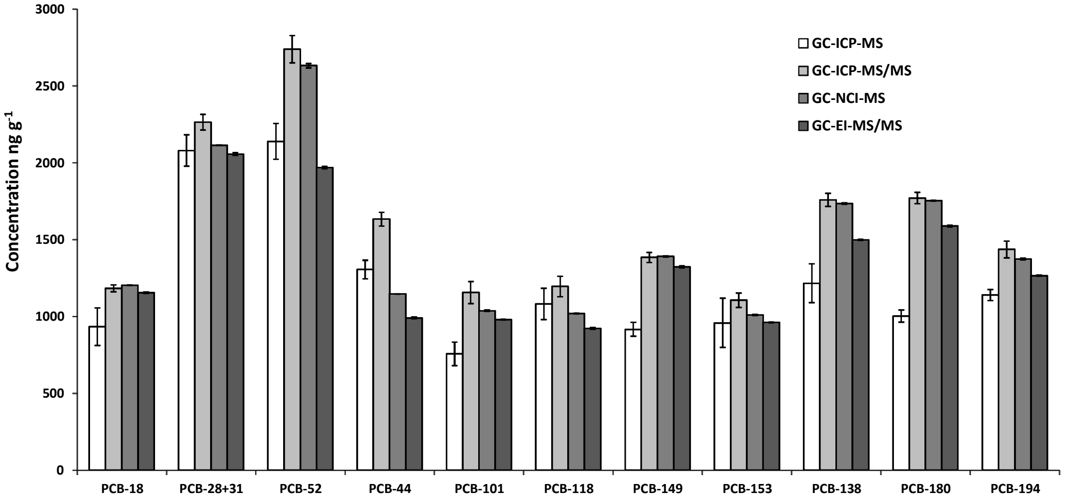


Figure 1. Concentration of the ^{37}Cl-labelled PCBs contained in the spike solution employed in this work calculated by reverse IDMS using four different techniques (GC-ICP-MS, GC-ICP-MS/MS, GC-NCI-MS and GC-EI-MS/MS). Error bars correspond to the standard deviation of three independent blends of the spike solution and the natural abundance standard containing all target congeners.

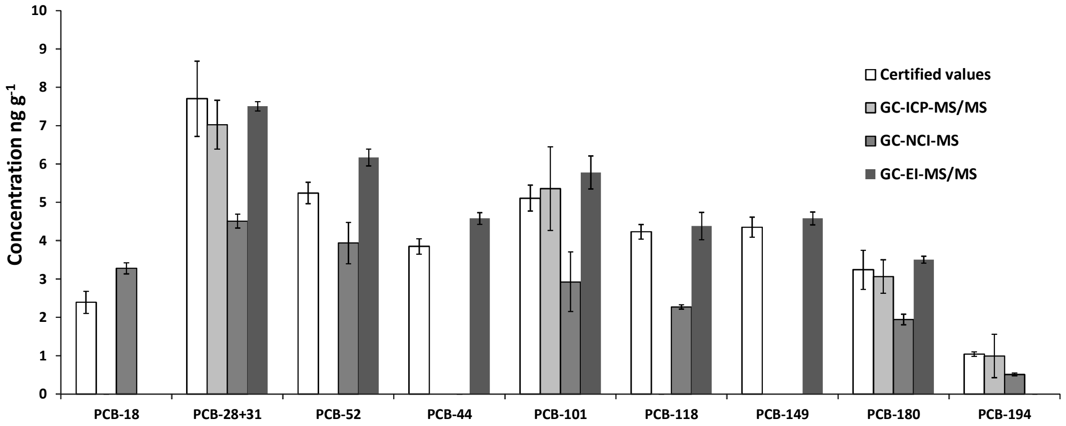


Figure 2. Comparison of the certified values and the experimental concentrations of the target PCBs obtained in the analysis of the SRM 1941 b (Organics in Marine Sediment) using three different techniques (GC-ICP-MS/MS, GC-NCI-MS and GC-EI-MS/MS). Error bars correspond to the standard deviations n=3 independent extractions.

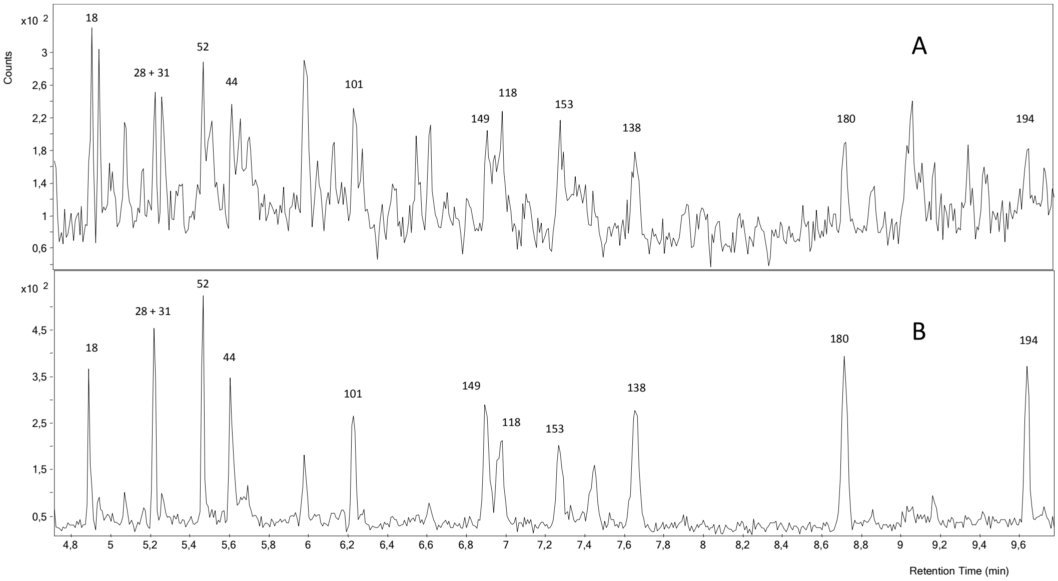


Figure 3. GC-ICP-MS/MS chromatogram of the certified reference sediment SRM 1941b spiked with the mixture of ^{37}Cl-labelled PCBs. A) chromatogram for transition 35Cl → 35Cl-H$_2$ and B) chromatogram for transition 37Cl→ 37Cl-H$_2$.

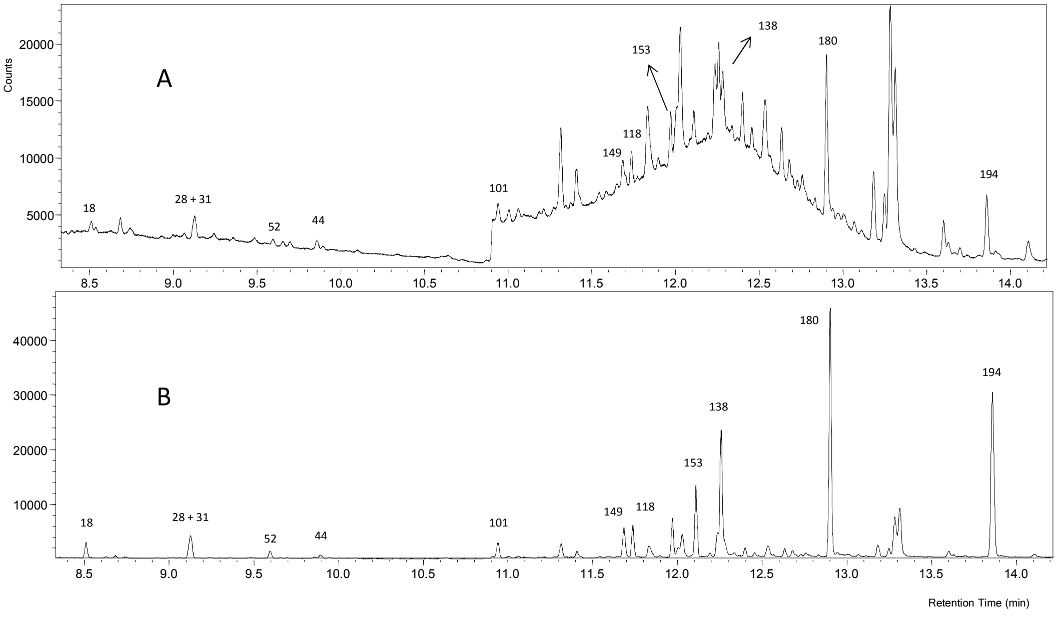


Figure 4. GC-NCI-MS chromatogram of the certified reference sediment SRM 1941b spiked with the mixture of ^{37}Cl-labelled PCBs. A) chromatogram for ^{35}Cl and B) chromatogram for ^{37}Cl.

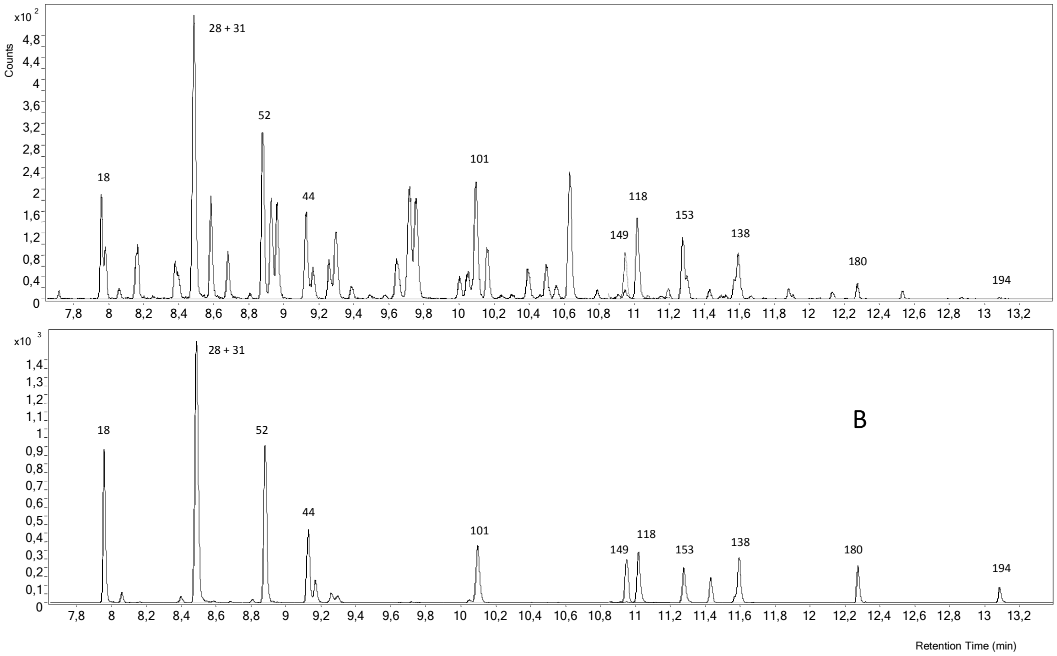
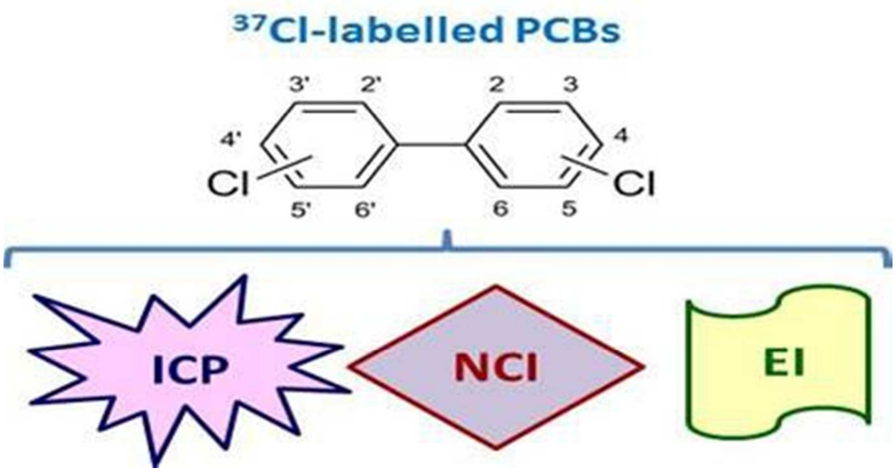


Figure 5. GC-EI-MS/MS chromatogram of the certified reference sediment SRM 1941b spiked with the mixture of ^{37}Cl-labelled PCBs. A) chromatogram of the transitions for the natural abundance PCBs and B) chromatogram of the transitions for the ^{37}Cl-labelled analogues.



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