Gas Chromatography-Mass Spectrometry: Application of New Findings in Analyzing Organochlorine Contaminants in a Candidate Food Reference Material

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Abstract

Organochlorines are common toxic contaminants in the food chain, especially in aquatic biota, thus leading the world population to undesired exposures. The chemical analyses of such trace pollutants may represent a challenge: if not properly conducted, they could suffer from great uncertainties. In the present work, a new candidate reference material of oyster tissue was analyzed for the content of organochlorines. This was done within the H2020 project PRO-METROFOOD to which 17 European Countries participated. Our laboratory strictly applied the international guidelines on the subject. Even by following the recommended guidelines, however, it is difficult to analyze some Polychlorobiphenyls (PCBs). The chromatographic coelution of Polychlorobiphenyls with the same degree of chlorination or coelutions between Polychlorobiphenyls different for one chlorine only (isobaric interferences), for example, is to be cited. For a reliable quantification, therefore, we usefully exploited some innovative findings recently made by us in the field of mass spectrometry: they allowed to achieve an optimum accuracy in the case of isobaric interferences so ensuring that a correct food safety assessment is carried out. When Polychlorobiphenyls are analyzed, there are a number of good reasons for maintaining the use of the electron capture detection (ECD) in combination with the mass spectrometry. However, the present study highlights the limits and the critical points of the approach using ECD only, as many laboratories do.

Keywords Food safety · Organochlorine contaminants · Candidate reference material · Oysters · Metrology · Gas chromatography-mass spectrometry (GC-MS) · Gas chromatography-electron capture detection (GC-ECD) · PCB isobaric interferences

Introduction

Organochlorines (OCs) such as organochlorine pesticides (OCPs) and Polychlorobiphenyls (PCBs) are chlorine-derived compounds enormously popular in the past and produced worldwide: the global production of DDT in 1974, for example, was 60,000 tons (WHO 1979).

Today OCs are ubiquitous and still detectable throughout the food chain, especially in seafood (Domingo and Bocio 2007; Smith and Gangolli 2002). This caused the Stockholm

Convention on Persistent Organic Pollutants (POPs) to enter into force on 2004: controlled disposal of organochlorines still available and global ban for use were proposed (Stockholm Convention on POPs 2004).

The high toxicity of these xenobiotics even in parts per billion makes their analysis a delicate matter. The need for a laborious purification step together with a perfect instrumental setting may lead to frequent large errors by non-specialized laboratories. As cited in a QUASIMEME performance study: "The bias obtained by the participating laboratories for the determination of PCBs and OCPs is currently too large to meet the requirements of international monitoring programmes" (De Boer and Wells 1996). One of the most effective ways to evaluate the laboratory performance and to correct possible critical points is the periodical analysis of a Certified Reference Material (CRM) as indicated by international guidelines (UNEP 2011).

Within the project PRO-METROFOOD that aimed to provide some pilot services (Rychlik et al. 2018), a material of

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oyster tissue was chosen as a candidate reference material and was delivered to our laboratory so that we made our analysis regarding the content of OCs. This material is to be considered important for standardization and harmonization and it represents a novelty since such reference materials are not currently available. One of the very few CRMs of this type is from NIST®, the National Institute of Standards and Technology (USA) that provides a material of oyster tissue, however, not certified for organochlorines (NIST, SRM 1566b n.d.). The situation is well summarized in a recent paper by the Institute for Reference Materials and Measurements (IRMM) discussing the EU Water Framework Directive. In that paper, it is said that "the lack of biota CRMs for the organic substances is confirmed" (Ricci et al. 2016).

Some analytical problems with organochlorines are historically known as arduous to be solved, even by applying the recommended guidelines (Qiu et al. 2017). In the present work are studied the chromatographic coelutions of PCB congeners different for one chlorine only, i.e., the so-called "isobaric interferences" (Guevremont et al. 1987; Frame et al. 1996; Ruddy et al. 2008; Barbounis et al. 2012; Megson et al. 2013). It is to be taken into account that the possible existing congeners of PCBs are 209 and no analytical column exists which is able to separate them all. Therefore such coelutions are likely to occur.

Contrary to the case of coeluting PCBs with the same degree of chlorination the high-resolution mass spectrometry is not affected by any error in the case of isobaric interferences.

However, the mass spectrometers that are much more widespread in laboratories are low-resolution ones and the present work solves the problem of isobaric interferences for analysts using low-resolution mass spectrometers as ion traps, single and the triple quadrupoles are.

Recently, we made important observations and developed innovative solutions in the field of mass spectrometry: they are able to achieve optimum accuracy also in the presence of isobaric interferences (Masci et al. 2015). In the present research, such innovations were applied for the first time to the very important coeluting couples PCB 114/153 and 157/180 simultaneously present in a certified sample: the quantification by means of the cited innovative method gave accurate results in the present study. It must be noted that PCB 114 and 157 are dioxin-like PCBs and that PCB 153 and 180 belong to the important "six indicators" as regulated by the European Union (Commission Regulation (EU) No 1259/ 2011).

Materials and Methods

Reagents and Chemical Standards

All reagents used were of pesticide grade. Acetonitrile, acetone, isooctane, n-hexane, petroleum ether 40–60 °C, toluene, methyl alcohol, dichloromethane, ethyl acetate, sodium

sulfate, and Florisil® 60–100 mesh were purchased from Carlo Erba Reagents® (Milan, Italy). The Supelclean LC-18 solid phase was from Supelco® (Bellefonte, PA, USA). Pure standards of OCPs and PCBs were purchased from different producers, mainly in solution form, along with their certificate of analysis. Certified solutions, as single standard or mixtures, were from Dr. Ehrenstorfer® (Augsburg, Germany), AccuStandard® Inc. (New Haven, CT, USA), Supelco® (Bellefonte, PA, USA), and Riedel-de Haen/Fluka/SIGMA ALDRICH® (Switzerland).

The Certified Reference Material "lyophilized Sea Water Mussel SQC068MUS-30G, lot LRAA9269" was from Sigma-Aldrich®. The certificate of the analysis of the CRM SQC068MUS-30G lot LRAA9269 is reported in the Supplementary Material.

Oyster Material to Be Analyzed

The oyster material to be analyzed was delivered in lyophilized form. OCs were searched and determined in three bottles (n. 37, 38, and 39) that were analyzed in triplicate. An empty bottle to be used in the blank analysis was delivered together with the material.

Sample Treatment and Preparation

About 2.5 g of lyophilized material was exactly weighed. The sample was subjected to a double purification step by using the solid phase extraction technique. In the first purification, diatomaceous earth and C18 were used, while in the second purification, the solid phase was constituted by Florisil®. The procedure was carried out in compliance with the Good Laboratory Practice in order to avoid cross contaminations or losses (false positives of false negatives). The procedure has been already described in any detail (Masci et al. 2014) and the only modification was in the centrifugation passage: 383 g for 10 min at 10 °C (four times).

Moisture content was measured by means of an oven-drying procedure at 105 °C.

Instrumental Analysis

The present work followed the recommendations issued by international bodies about the instrumentation requested for the determination of trace contaminants in food, so ensuring that each analysis was performed under metrological conditions. With this regard, samples under study were regularly double examined by means of two totally different detection systems.

Two identical capillary columns RTx®-PCB Restek (Bellefonte, PA, USA) 60 m × 0.25 mm ID, 0.25 μm df) were mounted on two separate injectors and were installed in the same gas chromatographic oven (Varian® 3800 GC). The first column was connected to an electron capture detector (ECD)

while the second was connected to the mass spectrometer Varian® Saturn 2000 that is Ion Trap–equipped. Instrumental conditions were as already reported (Masci et al. 2015). In each analysis, the sample was first injected in the ECD-column (GC-ECD) and then in the mass spectrometric-column (GC-MS). Calibrations were performed by using certified standard solutions of the OCs under study that were injected on both columns at appropriate concentrations (multi-level calibration).

The detailed instrumental analytical procedure is reported in the Supplementary Material, Figs. S1-S6.

Analytical Quality Control

The analysis of the new reference material was carried out within the routine activity of our laboratory that is specialized in the analysis of OCs. Internal and external controls for the performance of analytical work are conducted on a regular basis: recovery measures for all analytes, linearity of response, limit of detection (LOD), limit of quantification (LOQ), interlaboratory ring tests (FAPAS 2003), analysis of CRMs, use of certified authentic standards, blanks, traceability, and registration of work performed (Masci et al. 2014, 2015).

The limit of detection (LOD) and the limit of quantification (LOQ) are reported in Table 2.

One control was carried out in a targeted way, i.e., the analysis of a CRM purchased specifically for the present work (lyophilized mussels).

PCB 5 at 350 μg L^{-1}, PCB 198 at 500 μg L^{-1}, and 2,2′-DDE at 304 μg L^{-1} were used as surrogate internal standards. They were added to the sample as a 100 μL solution to monitor the trend of the analysis.

PCB 209 at 617.28 μg L^{-1} was used as a Syringe Internal Standard (Syringe IS): 100 μL was added to the final vial just before GC injection to correct possible variations in the injection volumes and in the retention times.

Blank was executed by using the ad hoc empty bottle delivered together with the reference material: no subtraction for blank was needed.

Instrumentation is continuously checked and maintained according to the temps established by the manufacturer and in response to any unexpected needs. No analyses are carried out if apparatus does not match the performances specified by the manufacturer.

Results and Discussion

Table 1 shows the performance achieved in the analysis of the Reference Material "lyophilized Sea Water Mussel SQC068MUS-30G, lot LRAA9269" from Sigma-Aldrich® which is certified for some priority PCBs. The substantial agreement between the measured values and the declared ones

Table 1 CRM SQC068MUS-30G: acceptance intervals and certified values compared with the values measured in the present work (n. of analyses = 2)

| Analyte	Unit	CRM SQC068MUS-30G		Measured values	
		Acceptance interval	Certified value	GC-MS measurement	ECD measurement
PCB 28	μg/kg	117–307	212 ± 7.42	174 ± 20	138 ± 3
PCB 52	μg/kg	66–174	120 ± 4.20	125 ± 10	104 ± 3
PCB 101	μg/kg	124–328	226 ± 7.91	213 ± 17	181 ± 4
PCB 118	μg/kg	63.3–167	115 ± 4.03	142 ± 0	133 ± 2
PCB 114	μg/kg	72.1–190	131 ± 4.59	148 ± 22	
PCB 138	μg/kg	117–309	213 ± 7.46	178 ± 14	
PCB 153	μg/kg	170–448	309 ± 10.8	267 ± 19	
PCB 157	μg/kg	109–287	198 ± 6.93	215 ± 23	
PCB 180	μg/kg	128–338	233 ± 8.16	234 ± 11	

may be noted. All results, both from MS and from ECD detector, fall within the acceptance intervals. As regards the certified values, it can be seen that the uncertainty intervals of GC-MS measurements overlap the uncertainty intervals of the certified values in five cases out of nine (PCB 52, 101, 114, 157, 180). In the other four cases, the extremes of the two intervals are close. For five PCBs, the measurement was only possible with the mass spectrometric detector: the reason is explained below.

To understand why some PCBs cannot be measured with the ECD detector in the mussel CRM, the case of PCB 153 and PCB 114 will be examined (Fig. 1).

Figure 2 represents gas chromatograms in full scan mass spectrometry. By injecting the CRM Mussel SQC068MUS-30G (see chromatogram a), a peak that is the sum of PCB 153 and PCB 114 was obtained in both detection systems. This is a coelution between a superior congener with an inferior one (hexa-Cl with penta-Cl) that is to say a coelution between "near homologs."

The ECD detector is useless in these particular cases since it is not able to distinguish the quantitative contribution of each of the two PCBs. There are, however, a number of good reasons to maintain the use of the ECD detector in combination with mass spectrometry, especially in a laboratory where both detectors are already present. In fact, ECD shows an exceptional sensitivity towards halogenated compounds, the linearity of response may be different from the one observed with MS, and factors affecting accuracy are not the same for

Fig. 1 PCB 153 and PCB 114 (IUPAC names: *2,2′,4,4′,5,5′-*Hexachlorobiphenyl and 2,3,4,4′,5-Pentachlorobiphenyl)
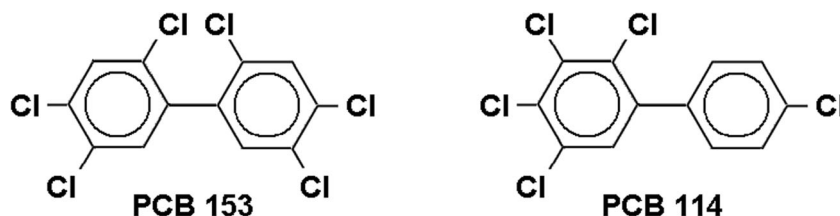
the two detectors. So a quantitative comparison between two different techniques may be useful. The problem is that many laboratories analyze PCBs with the use of ECD only (Halfadji and Touabet 2018; Kumar et al. 2018; Atmaca et al. 2019).

The present study highlights the limits and the critical points of the approach using the ECD only in the analysis of PCBs.

It is well known, instead, that mass spectrometry can quantify the superior Hexa-Cl congener (PCB 153) also in the presence of the coelution with the inferior Penta-Cl (PCB 114). In fact, in the mass spectrum of PCB 114, the ion 360 is not present as Fig. 2c clearly shows. Therefore, by selecting the molecular ion 360 m/z of PCB 153 (SIM mode or extracted ion mode) the problem can easily be solved.

In Fig. 3, it is displayed and integrated only the ion 360, both in the Mussel sample and in the calibration solutions: it is evident that the contribution of PCB 114 is zero and only PCB 153 is correctly quantified.

This is an already known procedure. On the contrary, the opposite operation, i.e., an accurate quantification of the inferior congener (PCB 114) in the presence of a superior congener (PCB 153) was commonly believed as unfeasible, even by

using mass spectrometry (Guevremont et al. 1987; Frame et al. 1996; Ruddy et al. 2008; Barbounis et al. 2012; Megson et al. 2013). With reference to Fig. 2, it was mistakenly thought that the dechlorination ionic cluster around 325–327 m/z, present in PCB 153, could interfere with the molecular ionic cluster of PCB 114 around 324–328 m/z. In mass spectrometry, the interference between ion fragments of different type and origin, but with the same nominal mass, is called "isobaric interference" (Meija and Caruso 2004).

In our 2015 research (Masci et al. 2015), we corrected this erroneous belief about PCBs. We highlighted that all PCBs have an alternation of even-odd ion clusters, as Fig. 2 shows. The first dechlorination cluster 325–327 m/z of PCB 153 does not contain even ions in an appreciable way, while the molecular ion cluster of PCB 114 does not contain odd ions in an appreciable way. We experimentally demonstrated that by selecting the molecular ion of the inferior congener, the quantification can be achieved with no errors. Therefore, the supposed isobaric interference between near homolog PCBs does not exist in an appreciable way.
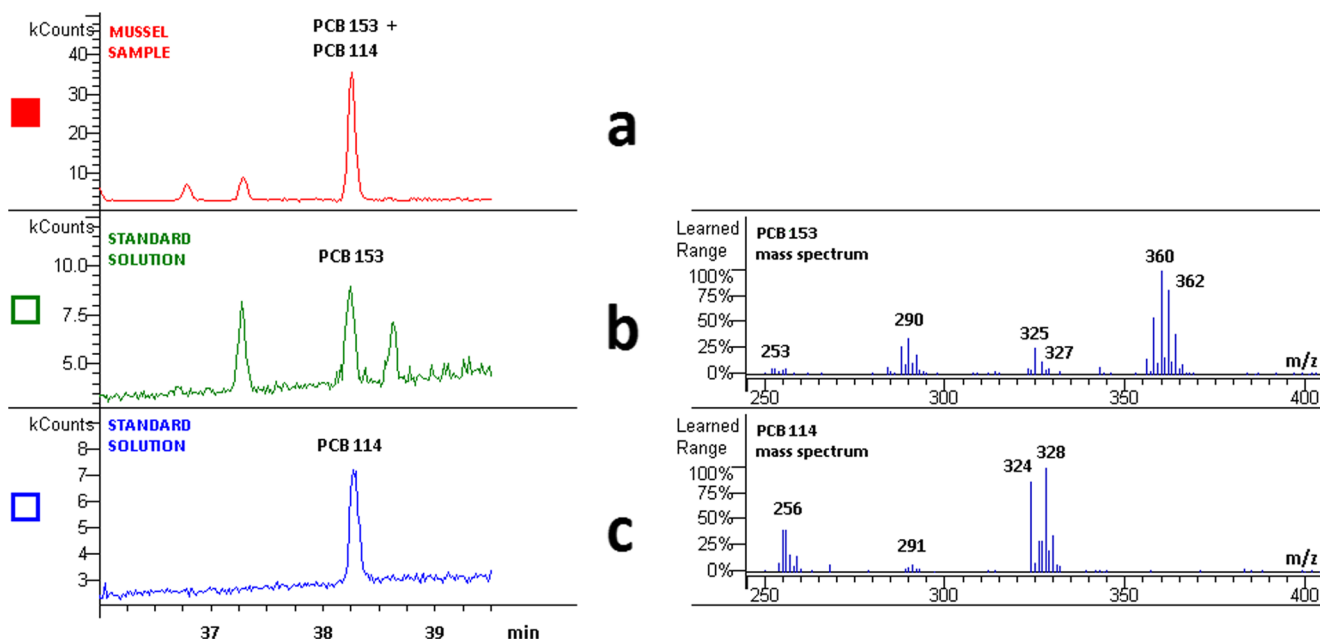
Fig. 2 On the left: gas chromatograms in full scan mass spectrometry. **a** CRM Mussel SQC068MUS-30G from Sigma-Aldrich®. **b** Standard mix solution with PCB 153. **c** Standard solution of PCB 114. On the right: Mass spectra of PCB 153 and PCB 114
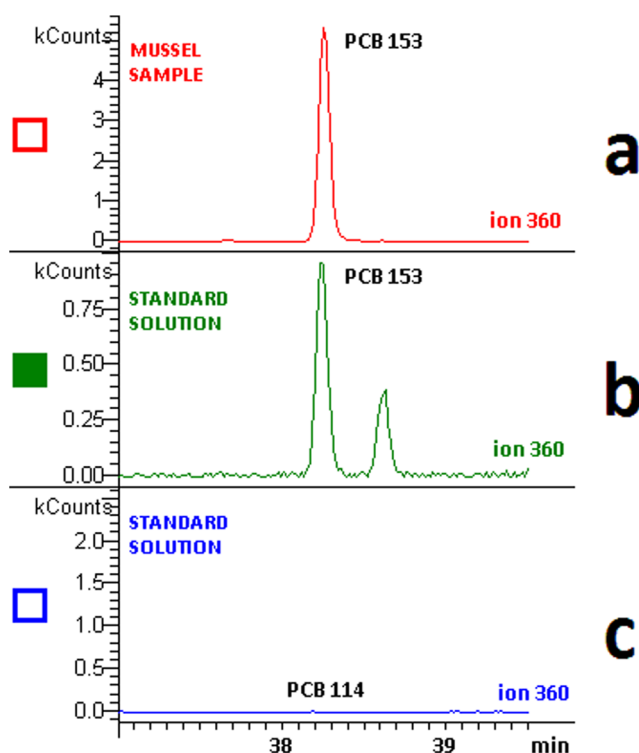
Fig. 3 Gas chromatograms of Fig. 2 in extracted ion mode (ion 360). **a** CRM Mussel SQC068MUS-30G. **b** Standard mix solution with PCB 153. **c** Standard solution of PCB 114

Fig. 4 Gas chromatograms of Fig. 2 in extracted ion mode (ion 328). **a** CRM Mussel SQC068MUS-30G. **b** Standard mix solution with PCB 153. **c** Standard solution of PCB 114

This concept is valid for all possible PCB coelutions of near homologs.

In Fig. 4, the analysis of PCB 114 in the CRM SQC068MUS-30G is reported.

By integrating the molecular ion 328 m/z of PCB 114, the contribution of PCB 153 is zero. The good accuracy of the procedure was confirmed by comparing the measured values and the certificate of analysis for PCB 114 and PCB 153. This is the only possible way to determine PCB 114 in the CRM, at least with low-resolution mass spectrometry and in the presence of the coelution (that is likely to occur: we note that the analytical column here used is very specific for PCBs, with high-resolution power (Megson et al. 2013)).

The same approach was applied for another coelution of near homologs observed in the CRM Mussel SQC068MUS-30G: PCB 157 and PCB 180. It is to be mentioned that PCB 114 and PCB 157 are very important congeners belonging to Dioxin-like PCBs (Commission Regulation (EU) No 1259/ 2011).

The identical procedure was usefully exploited also for the oyster material to be analyzed within the project PRO-METROFOOD. In Fig. 5, the GC-MS chromatogram of the oyster material in the bottle n.39 is displayed three times: every time it is recalled a different ion or cluster of ions.

In chromatogram a, the ion 360 is displayed and therefore there is the certainty that PCB 153 is present. In
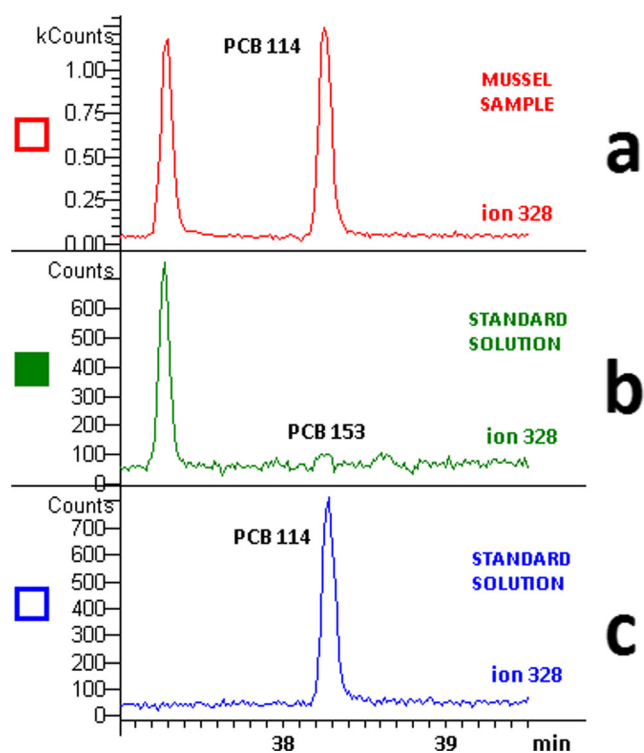
chromatogram b, the ionic cluster 324 + 325 + 326 + 327 + 328 is displayed and a peak can be observed. According to the "historical" old belief of PCB isobaric interferences, nothing could be said because the peak could come from the dechlorination cluster of PCB 153 plus the molecular ion of PCB 114 since they chromatographically coalesce.

In chromatogram c, there is the evident application of the concept exposed above: by recalling the ion 328, typical only of PCB 114 and not of PCB 153, there is the absolute certainty that PCB 114 is absent in the oyster material, more precisely below the declared LOD of 0.3 μg/kg (Table 2). Therefore, the peak in Fig. 5b derives from PCB 153 only (more precisely from the dechlorination odd fragments 325 e 327 m/z).

The same method was applied for the coelution of the near homologs PCB 157 and PCB 180: PCB 157 was found to be absent in the oyster tissue (below the LOD of 0.4 μg/kg).

It is now clear why in Table 1 only GC-MS results are reported for five PCBs in the CRM SQC068MUS-30G: the coelutions 114/153 and 157/180 make it useless the ECD detector. In addition, PCB 138 was seen to be interfered by the signal of another organochlorine so making usefully exploitable only the mass spectrometric analysis for it.

Table 2 shows the analysis of the candidate reference material as carried out in our laboratory. A total of 29 organochlorines, which comprised of eight pesticides and 21 PCBs, were searched and analyzed. With the
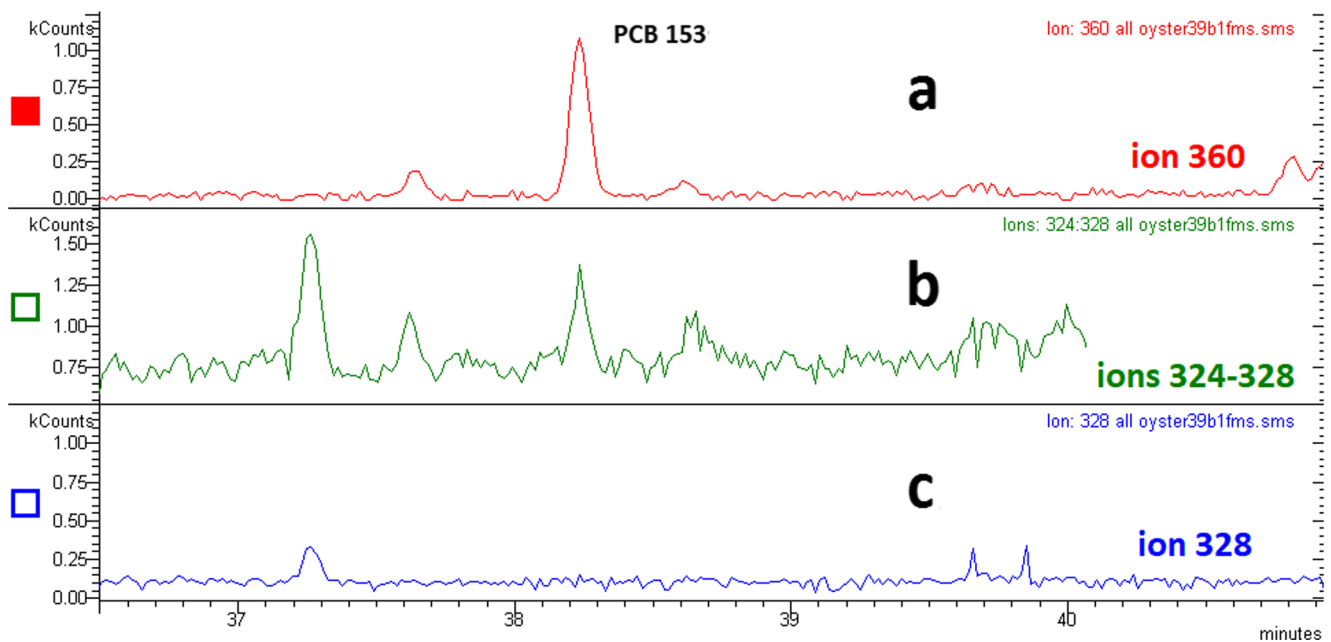
Fig. 5 Gas chromatogram-MS of the oyster material to be certified. Bottle n.39. Extracted Ion mode. **a** Ion 360. **b** Cluster 324–328. **c** Ion 328

exception of octachlorostyrene, all of the analytes are listed under the Stockholm Convention on POPs, 2004. Among the 21 PCBs, they are comprised of the "six EU indicators", three Dioxin-like PCBs (Commission Regulation (EU) No 1259/ 2011), and the "seven ICES PCBs" (Webster et al. 2013).

We ascertained that the lyophilized material delivered to us derived from fresh oysters with OC contaminant levels similar to the ones generally observed in these bivalve mollusks, which have a limited bioaccumulation power: the scarce bioaccumulation of POPs is to be attributed to the low lipid content.

For example, the sum of the seven ICES PCBs (PCB 28, 52, 101, 118, 138, 153, 180) in the delivered lyophilized material has a mean value of 36.9 μg/kg (Table 2). By taking into account that in the lyophilization process there was a well-defined concentration factor (moisture content in fresh oysters: about 90% (Orban et al. 2004), moisture measured in the delivered lyophilized material: 4.36%), we can deduce that in the fresh oysters, from which the material was derived, the sum of the seven ICES PCBs was about 4 μg/kg.

Previous studies of OCs in fresh oysters detected similar values for the sum of the seven ICES: 2.95–11.41 μg/kg (Dodoo et al. 2013) and 0.82–1.20 μg/kg (Orban et al. 2004).

Not even these low levels, however, can be considered safe for health since at the moment, studies on the subject indicate there is no concentration of such xenobiotics, albeit low, that can be considered safe for human health. In the case of those contaminants which are considered to be genotoxic carcinogens (as OCs are) EU regulation suggests that "maximum levels should be set at a level which is As Low As Reasonably Achievable (ALARA)" (Commission Regulation (EC) No 1881/ 2006).

Conclusions

A new candidate reference material of oyster tissue was analyzed in our laboratory for the content of organochlorines as toxic contaminants. Such pilot service in the context of the H2020 project PRO-METROFOOD is to be considered of strategic relevance since there are no currently available reference materials for bivalve mollusks which are certified for organochlorines.

As expected, the analysis has needed quality controls and good laboratory practice at the "state-of-the-art" level. It is known, however, that some analytical problems are difficult to be faced, even by applying the international guidelines in the field. One critical point was represented until now by the so-called "isobaric interferences" when studied in low-resolution mass spectrometry.

To face this problem, we used an innovative approach in the field that was recently introduced by us: for the first time, it was applied on a matrix in which two isobaric couples of important dioxin- and non-dioxin-like PCBs are completely coalescent.

The approach confirms itself effective in correcting a wrong belief widespread in literature.

In the present study, some drawbacks deriving from the use of the ECD detector only, in the field of PCB analysis, have been experimentally demonstrated.

Table 2 Analysis of the candidate reference material "oyster tissue" (µg/kg)

Analyte	Bottle 37 measur. no. 1	Bottle 37 measur. no. 2	Bottle 37 measur. no. 3	Bottle 37 mean	Bottle 37 st. dev.	Bottle 38 measur. no. 1	Bottle 38 measur. no. 2	Bottle 38 measur. no. 3	Bottle 38 mean	Bottle 38 st. dev.	Bottle 39 measur. no. 1	Bottle 39 measur. no. 2	Bottle 39 measur. no. 3	Bottle 39 mean	Bottle 39 st. dev.	LOD	LOQ
4,4'-DDE	3.08	3.12	2.48	2.89	0.36	5.53	3.30	3.39	4.07	1.26	3.76	3.32	4.06	3.71	0.37	0.03	0.06
cis-Chlordane	0.05	0.05	0.09	0.06	0.02	0.11	0.08	0.11	0.10	0.02	0.07	0.07	0.09	0.08	0.01	0.02	0.03
trans-Chlordane	0.09	0.08	0.05	0.07	0.02	0.08	0.09	0.12	0.10	0.02	0.03	0.03	0.04	0.03	0.01	0.02	0.03
cis-Nonachlor	0.03	0.06	0.03	0.04	0.02	<0.03	0.04	0.04	0.04	0.00	0.06	0.05	0.05	0.05	0.01	0.02	0.03
trans-Nonachlor	0.16	0.18	0.14	0.16	0.02	0.23	0.20	0.25	0.23	0.03	0.26	0.22	0.28	0.25	0.03	0.02	0.03
Hexachlorobenzene	0.21	0.16	0.11	0.16	0.05	0.06	0.05	0.05	0.05	0.01	0.07	0.10	0.06	0.08	0.02	0.02	0.05
Octachlorostyrene	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.03	0.05
Mirex	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.04	0.06
PCB 52	1.9	1.8	1.5	1.7	0.2	2.4	2.0	2.0	2.1	0.2	2.5	2.1	2.6	2.4	0.3	0.05	0.2
PCB 151	1.8	2.0	1.5	1.8	0.2	2.2	2.0	1.8	2.0	0.2	2.4	2.1	2.6	2.4	0.2	0.1	0.2
PCB 28	0.5	0.4	0.3	0.4	0.1	0.5	0.4	0.4	0.4	0.1	0.5	0.4	0.5	0.5	0.1	0.04	0.1
PCB 44	0.5	0.5	0.4	0.5	0.1	0.6	0.6	0.5	0.6	0.1	0.6	0.5	0.6	0.6	0.1	0.04	0.1
PCB 47	0.7	0.8	0.6	0.7	0.1	1.1	0.9	0.7	0.9	0.2	0.7	0.6	0.7	0.7	0.1	0.04	0.1
PCB 49	1.0	1.0	0.6	0.9	0.2	1.1	1.4	1.1	1.2	0.2	1.2	0.9	1.2	1.1	0.2	0.04	0.1
PCB 66	0.6	0.6	0.6	0.6	0.0	0.8	0.6	0.6	0.7	0.1	0.7	0.6	0.7	0.7	0.1	0.04	0.1
PCB 163	2.8	2.8	2.3	2.6	0.3	5.0	2.8	2.7	3.5	1.3	3.3	2.9	3.6	3.3	0.3	0.1	0.2
PCB 87	0.79	0.80	0.64	0.74	0.09	0.77	0.77	0.72	0.75	0.03	0.74	0.63	0.80	0.72	0.09	0.03	0.06
PCB 97	0.9	1.0	0.9	0.9	0.1	1.2	1.0	1.0	1.1	0.1	1.0	0.9	1.1	1.0	0.1	0.04	0.1
PCB 101	5.2	5.2	3.8	4.7	0.8	6.4	5.6	5.5	5.8	0.5	5.0	4.2	5.3	4.8	0.6	0.04	0.1
PCB 114	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.3	0.5
PCB 118	4.1	4.1	3.8	4.0	0.2	4.7	4.5	4.5	4.6	0.1	4.5	4.0	5.0	4.5	0.5	0.04	0.1
PCB 138	7.4	5.0	7.3	6.6	1.4	6.9	5.1	5.1	5.7	1.0	9.2	7.3	8.4	8.3	0.9	0.3	0.6
PCB 153	16.8	16.0	13.1	15.3	1.9	18.3	17.4	17.8	17.8	0.4	17.0	14.3	18.4	16.6	2.1	0.1	0.2
PCB 157	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.4	0.7
PCB 170	0.4	0.5	0.2	0.4	0.1	0.3	0.2	0.2	0.2	0.1	0.3	0.2	0.2	0.2	0.1	0.1	0.2
PCB 180	1.4	1.4	1.3	1.4	0.1	1.6	1.4	1.5	1.5	0.1	1.5	1.3	1.7	1.5	0.2	0.1	0.2
PCB 187	5.6	5.6	4.3	5.2	0.7	5.8	5.7	5.6	5.7	0.1	5.4	4.5	5.9	5.3	0.7	0.1	0.2
PCB 194	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.1	0.2
PCB 206	<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			<LOD	<LOD	<LOD			0.2	0.3

Compliance with Ethical Standards

Conflict of Interest Maurizio Masci declares that he has no conflict of interest. Teresina Nevigato declares that she has no conflict of interest. Roberto Caproni declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Not applicable.

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