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Short communication

Selective determination of polychlorinated biphenyls in waste oils using liquid–liquid partition followed by headspace solid-phase microextraction and gas chromatography with atomic emission detection

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Abstract

A procedure for the determination of the total content of polychlorinated biphenyls (PCBs) in industrial oil samples using gas chromatography coupled to atomic emission detection (GC–AED) is presented. Analytes were extracted from the samples using dimethylsulfoxide (DMSO), this extract was diluted with water, and PCBs were concentrated on a PDMS–DVB solid-phase microextraction (SPME) fibre using the headspace (HS) mode. Fibres were thermally desorbed for 3 min in the splitless injection port of the GC–AED system. Influence of liquid–liquid extraction conditions on the performance of the analytical procedure is presented and the need of a sample oxidation step, previous to the extraction of the PCBs with DMSO, discussed. Working under optimal conditions, quantification limits from 0.5 to 1 μg/g (total PCBs content) were obtained for several Aroclor mixtures in transformer oil samples. The repeatability of the whole sample preparation procedure (liquid–liquid partition followed by headspace SPME and GC–AED determination) ranged from 4 to 7%.

Keywords: Oils; Headspace analysis; Solid-phase microextraction; Polychlorinated biphenyls; Dimethylsulfoxide

1. Introduction

Nowadays, due to their toxicity and environmental persistence, the industrial production and applications of PCBs have been restricted [1]. However, in the recent past, they were used as thermal and electrical insulating additives in industrial oils (particularly in transformer oil) at high concentration levels [2,3]. According to European regulations, electrical transformers using insulating oils with a total PCB content higher than 50 μg/g, can be employed until the end of their useful life; however, those oil samples require to be identified and labelled as PCBs mixtures for a proper waste disposal [4].

Analytical determination of PCBs in oil is a hard task due to their affinity for the matrix and the high number of interferences contained in the sample. Thus, relatively complex, solvent and time consuming sample preparation schemes involving the use of normal phase sorbents and gel permeation chromatography have been proposed for their isolation from oil samples, previously to the gas chromatographic analysis of the purified extracts [3,5,6]. An alternative sample preparation approach consists of oil dilution with *n*-hexane followed by the extraction of PCBs using an aprotic and water miscible solvent, e.g. acetonitrile, dimethylformamide or dimethylsufoxide, which show the capacity to establish π–π interactions with the aromatic ring of the analytes [7–11]. Previous to the application of this procedure, some authors had recommended an oxidative treatment of the oil matrix with sulphuric acid [12]. Analytical determination of the extracted compounds is normally performed using GC–ECD or GC–MS. Alternatively to both techniques, GC–AED shows an excellent selectivity for chlorinated species [13]; therefore, it could be potentially used for the analysis of PCBs in oil matrices reducing the number of clean-up steps involved in the sample preparation procedure. The only drawback associated to the GC–AED technique is the relatively poor sensitivity for chlorinated species (absolute detection limits from 200 to 500 pg). So, any procedure for the determination of PCBs in oil matrices using AED detection should include a pre-concentration step.

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Recently, solid-phase microextraction (SPME) has been proposed as a simple and effective technique for the selective headspace (HS) extraction of PCBs from water and aqueous lixiviates from solid matrices [14–16]. For aqueous samples, the achieved pre-concentration factors using non polar fibres (e.g. PDMS and PDMS–DVB) are very high; however, the affinity of PCBs for the SPME fibre decreases dramatically when organic samples, such as oil matrices, are considered.

The aim of this paper is the development of a simple procedure to determine the global PCB content in waste oil samples. Analytes were firstly extracted from the sample using DMSO, concentrated on a non-polar SPME fibre and selectively detected using a GC–AED system. The influence of different sample treatments, previously to the SPME step, on the selectivity and sensitivity of the method is described.

2. Experimental

2.1. Apparatus

Chromatographic separations were performed using an Agilent (Wilmington, DE, USA) Model 6890 Series Plus gas chromatograph equipped with a split/splitless injection port and electronic pressure control. Detection was achieved with an Agilent G2350A atomic emission detector. Data were acquired using the Agilent Chemstation software (revision A.05). PCBs were separated on a DB-5 type capillary column (30 m × 0.25 mm i.d., d.f.: 0.25 μm) purchased from J&W Scientific. Helium was used as both carrier gas in the column (at a constant flow of 1.5 ml/min) and make-up gas in the microwave induced plasma (60 ml/min). O_2 (99.99%) was added as auxiliary gas to the plasma at a pressure of 20 psi. SPME fibres were desorbed in the GC injection port for 3 min at 260 °C. The splitless time was 3 min and the GC oven was heated using the following program: 3 min at 90 °C, first ramp at 20 °C/min to 170 °C (held for 7.5 min), second ramp at 3 °C/min to 250 °C (held for 5 min). The transfer line and the detector cavity block were kept at 260 °C. Chromatograms were simultaneously monitored at the emission lines of chlorine (480.19 nm) and carbon (495.72 nm).

A manual SPME fibre holder was obtained from Supelco (Bellefonte, PA, USA). One-hundred μm PDMS and 65 μm PDMS–DVB microextraction fibres were also obtained from Supelco.

2.2. Reagents, standards and samples

n-Hexane and dimethylsulfoxide for trace analysis were obtained from Merck (Darmstadt, Germany), concentrated sulphuric acid was also obtained from Merck. A standard mixture of several CBs (2,4,4′-trichlorobiphenyl CB 28; 2,2′,5,5′-tetrachlorobiphenyl CB 52; 2,2′,3,4,4′,5′-hexachlorobiphenyl CB 138; 2,2′,4,4′,5,5′-hexachlorobiphenyl CB 153; and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl CB 180) in isooctane, was obtained from Supelco. 2,2′,4,5,5′-Pentachlorobiphenyl CB 101 was purchased from Dr. Erhendorfer. Aroclor mixtures: 1242, 1248, 1254 and 1260, with a total PCB concentration of 1000 μg/ml, in isooctane, were obtained from Supelco. Mixtures of individual congeners and dilutions of the Aroclor solutions were prepared in *n*-hexane.

Transformer oil samples were obtained from the local electricity supplier company. A sample of an industrial lubricating oil was also used to evaluate the efficiency of the proposed sample preparation method with a different oil matrix. Reference material BCR CRM 449 with a certified concentration of several PCBs was purchased from the Institute for Reference Materials and Measurements (Geel, Belgium).

2.3. Extraction procedure

Spiked and non spiked oil samples (0.5 ml) were diluted to 6 ml using *n*-hexane and treated with 10 ml of concentrated sulphuric acid for 10 min. The acidic extract was removed and analytes were extracted from the organic phase using 7 ml of DMSO. This extract was washed with 10 ml of *n*-hexane and the hexane layer discarded. Then, 5 ml of DMSO were transferred to a 110 ml vial and diluted with an appropriate water volume. The microextraction was performed in the headspace mode for 50 min, using a PDMS–DVB fibre, after adjusting the extract to 100 °C. Experimentally, it was found that the addition of sodium chloride, together with a certain volume of ultrapure water, to the SPME vessel increased the amount of PCBs transferred to the SPME fiber. The maximum yield was achieved for a 1:4 DMSO:water ratio (5 ml of DMSO extract plus 20 ml of water containing 300 mg of sodium chloride per ml). Under these conditions, the 65 μm PDMS–DVB fibre gave a higher extraction efficiency than the 100 μm PDMS one for the most volatile congeners. Globally, around 25% of the analytes in the sampling vessel were transferred to the SPME fibre using the above described conditions.

3. Results and discussion

3.1. DMSO extraction of PCBs from oil samples

Optimisation of the oil–DMSO partition conditions was carried out using samples spiked with commercial Aroclor mixtures (1242, 1248, 1254 and 1260), instead of individual congeners. In these experiments, 0.5 ml of oil were diluted to 6 ml with *n*-hexane, in order to facilitate phases separation after the addition of DMSO.

Initially, samples were extracted with 7 ml of DMSO in a separation funnel for 5 min and 5 ml of the DMSO layer directly submitted to the microextraction procedure. Under these conditions, a high number of interferences were co-extracted with the analytes to the DMSO phase and a

huge hump was observed in the chromatogram monitored at the carbon emission wavelength. This hump disturbed the stability of the baseline in the chlorine channel, causing a poor sensitivity and broad peaks for the PCBs, figure not given.

For avoiding these interferences, different modifications were introduced in the sample preparation scheme previously to the HS SPME step: oil oxidation for 10 min with 10 ml of concentrated sulphuric acid prior DMSO partition (1); removal of co-extracted compounds from the DMSO extract using 10 ml of *n*-hexane (2); and combination of both treatments (3). Considering four Aroclor mixtures and two different samples (transformer and lubricating oil), it was found that, the sum of peak heights for the most intense signals in the chlorine channel (between 8 and 12 peaks were integrated depending on the mixture), using sample treatments numbers 1 and 2 represented around 25 and 80% of the value obtained with the last one. Chromatograms, monitored at the carbon and chlorine channels, for transformer oil samples spiked with the Aroclor 1242 mixture and processed using the three above described extraction strategies are presented in Fig. 1. Washing of the DMSO extract with *n*-hexane (Fig. 1B) led to a cleaner chromatogram than oil oxidation with sulphuric acid (Fig. 1A); however, an unknown and intense peak (retention time around 20 min) was observed in the carbon channel (Fig. 1B). This peak interfered in the detection of several congeners in the chlorine channel. The combination of both sample treatments removed this discrete peak and the wide hump which appeared at the beginning of the carbon chromatogram (Fig. 1C). In view of those results, to increase the selectivity and the sensitivity of the proposed method, both: oil oxidation and washing of the DMSO extract, previously to the SPME step, were included in the sample preparation scheme.

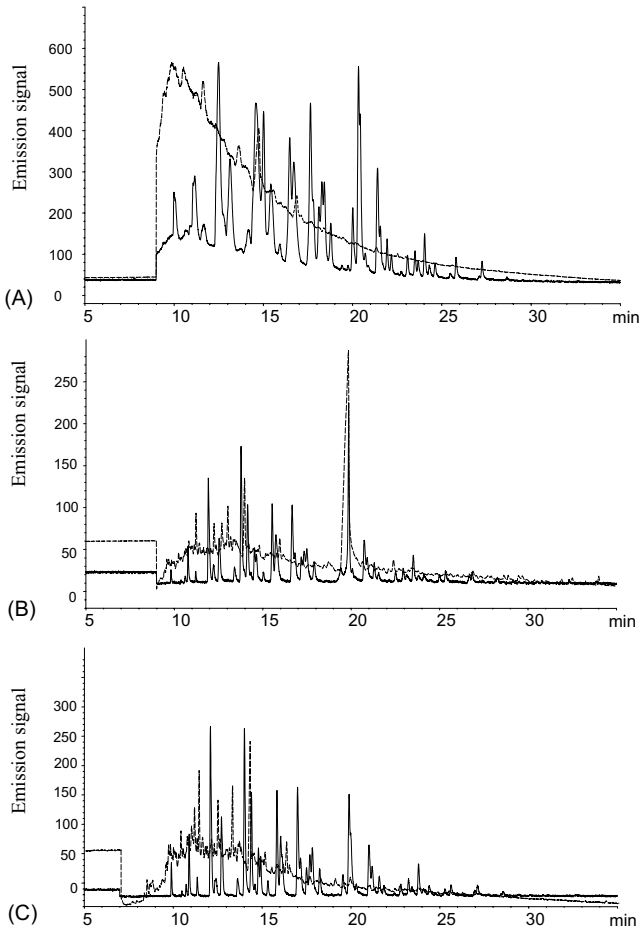

Fig. 1. GC–AED chromatograms for a transformer oil sample spiked with the Aroclor 1242 mixture and processed using different extraction strategies. (A) Oxidation with sulphuric acid previously to the DMSO extraction. (B) Washing of the DMSO extract with *n*-hexane before microextraction. (C) Combination of both procedures. Added concentrations 50 μg/ml (A) and 10 μg/ml (B and C). Dotted line, carbon emission channel; solid line, chlorine emission channel.

3.2. Analytical performance

GC–AED chromatograms obtained for two samples of transformer oil spiked with the Aroclor 1254 mixture at the same concentration level (10 μg/ml) are presented in Fig. 2. After sample extraction using DMSO, one of the extracts was diluted with water and analytes concentrated on a PDMS–DVB fibre for 50 min. The other one was made up to 100 ml with water, extracted three times with 10 ml of *n*-hexane and the combined extracts blown down to 0.1 ml using a gentle stream of nitrogen [7]. It is evident that the inclusion of the microextraction step in the sample preparation scheme improves the sensitivity of the method one order of magnitude and reduces the consumption of organic solvents.

The repeatability of the proposed procedure (DMSO extraction followed by SPME and GC–AED detection) was evaluated using transformer oil samples spiked with Aroclor 1242 and 1260 mixtures at two different concentration levels (5 and 25 μg/ml). Relative standard deviations between 4.2 and 6.5% were obtained for the sum of peak heights corresponding to the most intense signals (8 peaks for Aroclor 1242 and 10 in the case of Aroclor 1260) in chlorine chromatograms of both spiked samples. The linearity in the response was investigated using oil samples spiked with the same Aroclor mixtures at seven concentration levels between 1 and 100 μg/ml. Correlation coefficients (R^2) of 0.994 and 0.997 were obtained. Quantification limits were calculated for Aroclor concentrations which produced at least five peaks, in the chlorine channel, with a S/N ratio equal or higher than 10. Values of 1 μg/ml for Aroclors 1242 and 1248 and 0.5 μg/ml for Aroclors 1254 and 1260, were achieved.

Industrial oils with a certified total CBs content are not available, thus an attempt to validate the proposed method was made using the reference material CRM 449. This sample presents the typical profile of an Aroclor 1254 mixture, and contains certified concentrations for ten individual CB congeners. Aliquots of the reference material were diluted 10 times with *n*-hexane, and the concentrations of congeners

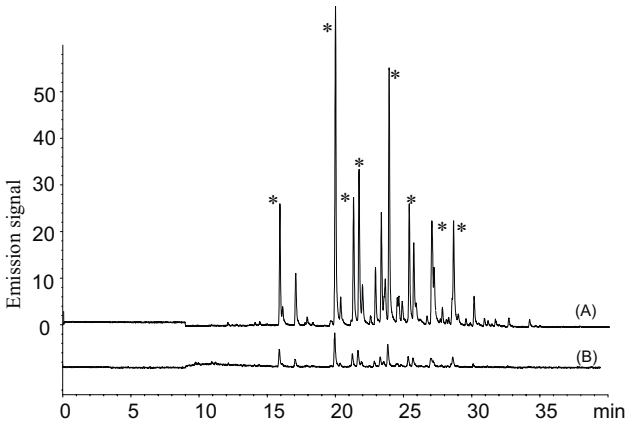

Fig. 2. GC–AED chromatograms at 480 nm for transformer oil samples spiked with Aroclor 1254 at the 10 μg/ml level and extracted with DMSO. (A) DMSO extraction followed by the concentration of PCBs on a PDMS–DVB fibre. (B) Dilution of the DMSO extract with water, reextraction of PCBs to 30 ml of *n*-hexane followed by evaporation to 0.1 ml and injection of 2 μl of this extract. Peaks used for quantitative purposes are labelled with and asterisk.

Table 1
Determination of CB congeners in CRM 449

CB congener	Concentrations (μg/g)	
	Certified	Found
28	0.8 ± 0.07	1.6 ± 0.2
52	31.4 ± 1.8	33 ± 3
101	57.2 ± 1.9	56 ± 5
153	39.0 ± 1.7	66 ± 6
180	10.4 ± 0.5	9.9 ± 0.6

28, 52, 101, 153 and 180 were determined using the standard addition method (three replicates of the zero level and two addition levels). In the case of CB 52, 101 and 180, a good agreement was found between measured and certified concentrations; however, for congeners 28 and 153 found values were clearly higher than the certified ones, Table 1. The source of this error is probably the coelution of several congeners in the same chromatographic peak. Using a BP-5 type capillary column, it is well known that CB 28 coelutes with the congener 31, and CB 153 with congeners 105 and 132 [17]. These interferent congeners (CBs 31, 105 and 132) are contained in the Aroclor 1254 mixture, and therefore in the analysed reference material.

3.2.1. Application to a real sample

The proposed method was applied to the quantification of the total PCBs in a contaminated transformer oil sample. The chlorine profile of this sample, matched with that of Aroclor 1254. The total PCB content was determined with the standard addition method using three aliquots of the native sample, and three aliquots spiked with increasing concentration (10, 20 and 40 μg/ml) of Aroclor 1254. The correlation coefficient of the standard addition curve was 0.995 and the total concentration in the sample was 80.5 ± 1.6 μg/ml, given as Aroclor 1254.

4. Conclusions

The proposed method combines the selectivity of the AED detector and the extraction efficiency of the SPME technique for the determination of the global PCB content in industrial oils, after a fast sample pre-treatment. Oil extraction with DMSO followed by a washing step using *n*-hexane, previously to the HS SPME, is the only required treatment for the screening of PCBs in oil samples, below the limits given by the European legislation. Levels of PCBs in polluted samples can be quantified using the standard addition technique, once the Aroclor profile is identified. In this case, it is advisable to include an oxidative step with sulphuric acid in the sample treatment. From our knowledge, the proposed method constitutes the first application of both SPME and AED to the analysis of PCBs in oil samples and it exhibits clear advantages in comparison to current methodology for this type of matrix and analytes.

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