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Focused ultrasound solid–liquid extraction of perfluorinated compounds from sewage sludge

María Pilar Martínez-Moral, María Teresa Tena*

Department of Chemistry, University of La Rioja. C/Madre de Dios 51, Logroño, La Rioja E-26006, Spain

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ABSTRACT

A method for the determination of perfluorocarboxylic acids (PFCAs) and perfluorooctanesulfonic acid (PFOS) in sewage sludge based on focused ultrasound solid–liquid extraction (FUSLE) and reverse-phase ultra-performance liquid chromatography (UPLC) coupled to quadrupole-time of flight mass spectrometry (QTOFMS) has been developed. FUSLE is a fast, low-cost and efficient extraction technique based on the application of high power focused ultrasonic waves using a micro-tip immersed directly in the extraction mixture.

For the method development, the extraction solvent was studied and afterwards the factors affecting the extraction efficiency were optimised by means of a central composite design. Optimal FUSLE conditions were: 8 mL of acetonitrile as extraction solvent and an ultrasonic irradiation power of 65% for only 20 s. Two extraction cycles were enough for the quantitative extraction of PFCs from sewage sludge. Limits of detection below 0.2 ng g^{-1} (dry sewage sludge), relative standard deviation values less than 8% and recovery values between 69 and 104% were found for the target analytes. Finally, the method was applied to the analysis of sewage sludge samples from several wastewater treatment plants of La Rioja.

1. Introduction

Perfluorocompounds (PFCs) have been widely used in different commercial and industrial applications such as paints, lubricants, PTFE synthesis, polishers and food packaging due to the fact that perfloroalkyl chains are oleophobic and hydrophobic and exhibit surface tension lowering properties. Because of the extensive industrial application and consumer use, PFCs such as perfluorocarboxylic acids (PFCAs), polyfluoroalkyl phosphate surfactants (PAPs), fluorotelomers (FTOHs), perfluorooctilsulfonamides (PFOSAs) and perfluoroalkyl sulfonates (PFASs) have been globally distributed. In addition, PAPs and FTOH, used as surface active agents in domestic products and in surface protection products for food contact coatings, may be atmospherically or metabolically degraded to PFCAs; and PFOSA breaks down to form PFOS. This fact means an increase of PFCAs and PFOS concentrations in the environment and an indirect source for human exposure [1–3].

The concern about PFCs occurrence in the environment has increased in the recent years because they are shown to be bioaccumulative and resistant to biological and chemical degradation and potentially harmful. They are also resistant to hydrolysis, photolysis and metabolic processes in living organisms. Increasing PFCA and PFOS concentrations in environmental samples, wildlife and humans, as well as biomagnification through food chains, have been reported [4,5]. PFOS and PFCAs have long half lives in humans and it has been proved that they exhibit toxicity in laboratory animals causing developmental toxicity carcinogenicity, liver cancer, affect the lipid metabolism and disturb the immune system [6].

Methods for the determination of PFCs in environmental and biological samples such as sewage sludge [7–11], water [12,13], sediments [14–16], molluscs [17], sunfish fillets [18] or biota [19] have been developed [20]. The accumulation in humans has been studied through the analysis of blood [20,21] or tissue [22]; furthermore the human exposure to sources such as articles of commerce [23], food and drinking water [24–27], food [28] and food packaging is also of interest [29–33].

The analysis of sewage sludge is important because of the information about chemical pollution in the aqueous environment and the risk associated with the reutilisation of sewage sludge as bio-solids for land application. However, it is a difficult task due to the complexity of the matrix and wide of variety of compounds which can act as interference in the analysis. Several methods for the determination of PFCs in sewage sludge have been reported, using ultrasound solid–liquid extraction (USLE) [7,15] or pressurised liquid extraction (PLE) [11] as extraction step, or the sewage sludge digestion [8,10] followed by a solid

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* Corresponding author. Tel.: +34 941 299 627; fax: +34 941 299 621.
E-mail addresses: maria-pilar.martinez@unirioja.es (M.P. Martínez-Moral), maria-teresa.tena@unirioja.es (M.T. Tena).

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phase extraction (SPE) clean up implying an extra solvent consumption and long-time analysis.

Focused ultrasound solid liquid extraction (FUSLE) is a relatively new technique based on the application of high power focused ultrasonic waves using a micro-tip immersed directly in the extraction mixture. When ultrasound waves cross the liquid solvent, numerous tiny gas bubbles (cavitation bubbles) are produced that implode and locally produce very high temperatures, pressures and velocities of solvent micro-jets. It has been successfully applied for determining persistent organic pollutants in biota [31], sediments [34,35], indoor dust [36] and recycled paper material [37]. In this work, a method based in FUSLE for the determination of PFCAs (perfluoroheptanoic (PFHpA), perfluorooctanoic (PFOA), perfluorononanoic (PFNA), perfluorodecanoic (PFDA), perfluoroundecanoic (PFUnA), perfluorododecanoic (PFDoA) acids) and perfluoroctanosulfonate (PFOS) in sewage sludge is developed in order to shorten analysis time. After a study of the compounds stability and the most appropriate solvent for FUSLE, the main variables that affect the extraction efficiency, such as power, time, solvent volume and number of successive extractions were studied. Once the method was optimised and characterised, several real samples from wastewater treatment plants of La Rioja were analysed.

2. Material and methods

2.1. Standards and materials

HPLC grade solvents (methanol, acetone and acetonitrile), LC–MS grade acetonitrile, methanol and formic acid were obtained from Scharlab (Barcelona, Spain). Standards of perfluoroheptanoic acid (PFHpA) perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA) and perfluorooctanesulfonic acid (PFOS) were provided by Sigma Aldrich (Madrid, Spain). The isotopically labelled perfluoro-*n*-[$^{13}C_8$]octanoic acid and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate standards (M8PFOA and MPFOS) from Wellington Laboratories Inc. (Guelph, ON, Canada) at a concentration of 50 μg mL^{-1}, were used as an internal standard for perfluorocarboxylic acids and perfluorooctanesulfonic acid, respectively. Cellulose filters (20 mm diameter) were purchased from Restek (Bellefonte, PA, USA).

2.2. Samples

Dehydrated sewage sludge samples were obtained from different waste-water treatment plants of La Rioja. The samples were frozen and protected from light.

Spiked samples at a concentration level of 50 and 16 ng g^{-1} of each analyte were used to optimise the FUSLE conditions and to study the features of the method, respectively. These samples were prepared by adding an analyte standard solution in methanol and the mixture was thoroughly homogenised. Then, the samples were freeze-dried, ground and stored in darkness at 4 °C.

2.3. Focused ultrasound solid-liquid extraction (FUSLE)

A SONOPLUS 2070 focused ultrasound system (20 kHz, 70 W) equipped with a MS73 titanium microtip was used. 0.5 g of sample was placed with 8 mL of acetonitrile in a 34-mm glass tube and internal standards (M8PFOA and MPFOS) were added. Then FUSLE was performed twice for 20 s, at a pulsation of 0.5 and 65% of power. Extractions were carried out at 0 °C in an ice-water bath.

After the extraction step, FUSLE extract was centrifuged for 5 min at 3000 rpm using an Orto Alresa Digicen centrifuge. The sample was washed twice with 4 mL of solvent each. Rinses were added to the extract and it was evaporated to dryness under a nitrogen stream using a Turbo Vap II concentrator (Zymark, Hopkinton, MA, USA). The residue was reconstituted in 2 mL of LC–MS grade methanol and extracts were filtered through a 0.2 μm nylon filter before the UPLC–MS/MS analysis.

2.4. Pressurised liquid extraction

An ASE200 accelerated solvent extractor from Dionex, furnished with 11-mL stainless-steel extraction cells, was used to perform PLE. Extraction cells were filled inserting two cellulose filters at the bottom of the cell, 1 g of anhydrous sodium sulphate and the sample were added and the cell was completely filled with anhydrous sodium sulphate. Finally, a cellulose filter was placed on top. Methanol was used as extraction solvent, and the PLE conditions were those reported by Llorca et al. [11]: a temperature of 70C at 100 bar and two extraction cycles of 1 min. After the extraction step, PLE extracts (ca. 15 mL) were evaporated to 0.5 mL under a nitrogen stream using a Turbo Vap II concentrator (Zymark, Hopkinton, MA, USA). The residue was reconstituted up to 2 mL of LC–MS grade methanol. Extracts were filtered through a 0.2 μm nylon filter before the UPLC–MS/MS analysis.

2.5. UPLC–MS/MS analysis

A Waters Acquity UPLC chromatograph (Milford, MA, USA), equipped with a Waters Acquity BEH C18 50 × 2.1 (i.d.) mm 1.7 μm particle size column and a Waters VanGuard precolumn of the same material, coupled to a Microtof-Q (Q-TOF) mass spectrometer from Bruker Daltonik (GMBH, Germany) with an electrospray interface was employed for the separation and quantification of PFCs. The chromatographic and mass spectrometry data were acquired with the software Data Analysis Version 4.0 from Bruker Daltonik (GMBH, Germany). The sample tray was held at 25 °C, and the column was maintained at 35 °C.

The chromatographic separation and QTOF detection were performed in 4 min under conditions reported elsewhere [30]. Mobile phase consisted of a 0.1 % formic acid-acetonitrile mixture (solvent A) and a 0.1% formic acid aqueous solution (solvent B). The flow rate was set at 0.45 mL min^{-1} and the injection volume was 5 μL. Electrospray ionization was carried out using a capillary voltage of 3500 V in negative mode. A coaxial nebulizer N_2 gas flow (9.0 L min^{-1}) at 200 °C and 3.0 bar of pressure around the ESI emitter was used to assist the generation of ions. The mass spectrometer was calibrated across the mass range of 50–1500 m/z using internal references. The collision energy was set at 10 eV for PFHpA, 12 eV for PFOA, PFUnA and PFDoA and 14 eV for PFNA, PFOS and PFDA. Quantification was performed by multiple reaction monitoring (MRM) and ion extraction. The precursor ion-product ion transitions used were 363.00–318.97 for PFHpA, 420.96–376.97 for MPFOA, 412.96–368.97 for PFOA, 462.96–418.96 for PFNA, 512.96–468.92 for PFDA, 562.96–518.95 for PFUnA and 612.95–568.95 for PFDoA. Ions 498.92 and 502.92 were extracted for PFOS and MPFOS quantification, respectively. A UPLC–MS/MS chromatogram of FUSLE extracts from a spiked real sample (50 ng g^{-1}), a real sample and a procedure blank are shown in Fig. 1.

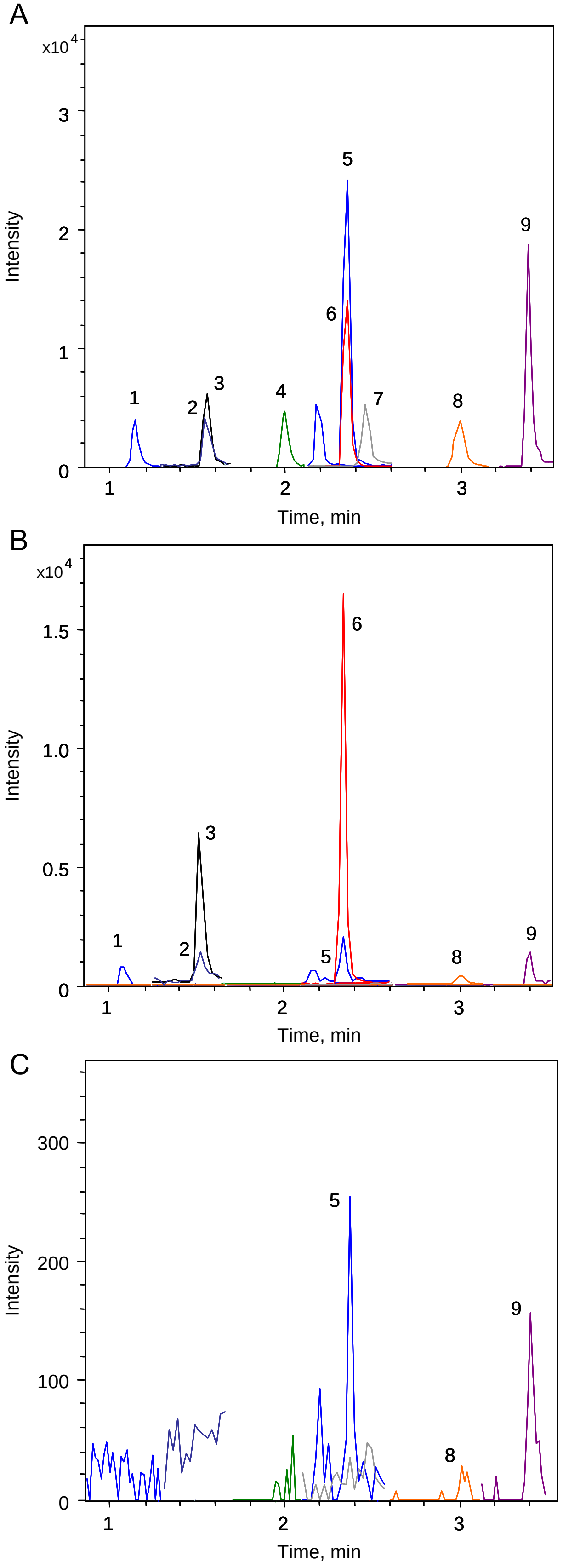

Fig. 1. UPLC–MS/MS chromatogram of (A). A FUSLE extract of a spiked sewage sludge sample (50 ng g^{-1}); (B) a FUSLE extract of a sewage sludge sample; (C) a blank. Peak identification: 1. PFHpA, 2. PFOA; 3. MPFOA; 4. PFNA; 5. PFOS; 6. MPFOS; 7. PFDA, 8. PFUnA and 9. PFDoA.

2.6. *Software for statistical analysis*

Experimental designs and statistical analysis were performed using Statgraphics Centurion XV (Statpoint, Herndon, VA, USA) and Microsoft Excel was used for drawing plots.

3. Results and discussion

3.1. *PFCs stability*

As FUSLE is a powerful extraction technique that implies high pressures and temperatures in the extraction solution, the first step was to assure the stability of the target compounds under FUSLE conditions. The study was performed, by applying intermediate FUSLE conditions (0.5 cycles, power of 75%, 0 °C) in triplicate to 9 mL of standard solution (100 ng mL^{-1} in methanol) during different times: 0, 20, 60 and 100 s. The extracts were analysed by UPLC–MS/MS. No statistical differences were found with irradiation time (ANOVA *p*-values between 0.194 and 0.663). Recoveries about 100% were achieved for all the extracts, so it can be concluded that there is not any degradation of the compounds during the FUSLE process.

3.2. *Study of FUSLE conditions*

The variables affecting the FUSLE process (extraction solvent, solvent volume, time and power) were studied in order to improve the efficiency of the extraction step.

3.2.1. *Solvent selection*

Five extraction solvents were tested: methanol, acidified methanol (0.1% acetic acid), 1:1 methanol:acetonitrile, 1:3 acetone:methanol and acetonitrile. The experiment was performed in triplicate. An aliquot of 0.5 g of spiked sewage sludge (each analyte concentration level of 50 ng g^{-1}) was extracted with 10 mL of solvent for 1 min at the same intermediate FUSLE conditions described above.

Fig. 2 shows that the signals were significantly higher with methanol, methanol:acetonitrile 1:1 or acidified methanol for PFHpA (*p*-value $3.2 \cdot 10^{-4}$), with methanol or acetonitrile for PFDA (*p*-value $2.2 \cdot 10^{-5}$) and with acetonitrile for PFUnA and PFDoA (*p*-values $5.5 \cdot 10^{-6}$ and $6.1 \cdot 10^{-7}$, respectively). Moreover, acetonitrile extracts were cleaner that the others as can be seen in the picture of the extracts provided in the electronic supplementary material (Fig. S1) and in the total ion chromatograms obtained for the different solvents (shown in Fig. 3).

Therefore, in order to improve the sensitivity of the method by increasing extraction efficiency (best with acetonitrile for all compounds but for PFHpA) and by decreasing the matrix compounds concentration, acetonitrile was chosen as extraction solvent for further experiments.

3.2.2. *Central composite design: Study of time, solvent volume and power*

A central composite design (CCD) was carried out to optimise solvent volume, time and power. The CCD consisted of a 23 factorial design with six star points located at ± α (α=1.68, for design rotatability) from the centre of the experimental domain and nine replicates of the central point. Solvent volume levels were 8, 9.6, 12 (c), 14.4 and 16 mL; time values were 20, 40, 70 (c), 100 and 120 s; and power values of 30, 42, 60 (c), 78 and 90% were tested. ANOVA results and Pareto charts (see Table S2 and Fig. S3 of the supplementary materials) showed that only time for PFDA (coefficient -3.00, *p*-value 0.030) has a significant effect on response. Thus, 20 s was set as extraction time and intermediate conditions were selected for power and solvent volume for further experiments: 65% and 8 mL of acetonitrile.

3.2.3. Study of the extraction cycle number

Finally, the last variable studied was the number of static extraction steps (cycles) required for complete extraction. The effect of 1, 2 or 3 extraction steps performed adding fresh solvent to the sample was studied. The extractions were performed in triplicate; the results are shown in Fig. S4 in the Supplementary materials (mean values ±95% confidence intervals). As can be seen, a second FUSLE step was necessary to improve recovery of some analytes up to 18–10%. However, no significant differences were found between two and three steps (*t*-test *p*-values between 0.21 and 0.75, >0.05). Therefore, two cycles of 20 s each were selected to extract PFCs from sewage sludge.

3.3. Features of the FUSLE–UPLC–MS/MS method

For the quantification of PFCs, the linearity of the method was studied in both methanol solution and sewage sludge extract in order to check the presence of matrix effects. Values are presented in Table 1. As can be seen, statistically significant differences were found between the slopes in methanol and sludge extracts for all analytes. The most important matrix effect was detected for PFDoA (Table 1). Therefore, quantification by means standard addition is proposed.

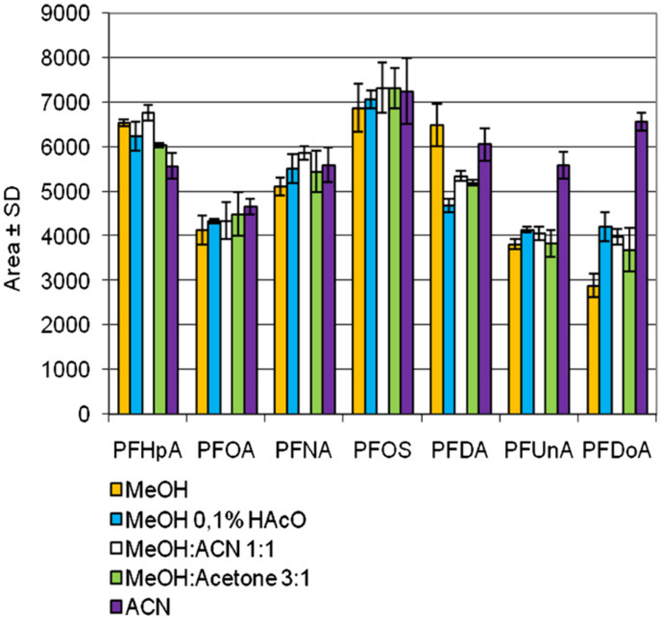

Fig. 2. Comparison of the response (peak area) obtained using different solvents (methanol, acidified methanol, methanol:acetonitrile 1:1, methanol:acetone 3:1 and acetonitrile) for FUSLE.

The limits of detection (LOD) and limits of quantification (LOQ) of the whole method were calculated as the concentration that provided a 3.3 or 10 signal-to-noise ratio (S/N), respectively. Limits of detection were between 0.06 and 0.2 ng g^{-1} (Table 2). In addition, the repeatability and intermediate precision (expressed as RSD,%) were calculated by ANOVA of three replicate extractions of a spiked sample (16 ng g^{-1}) for 3 days. As can be seen in Table 2, in all cases intermediate precision was below 8%. Finally a recovery study was carried out analysing four replicates of a spiked sample at 16 ng g^{-1} concentration to assess accuracy. A low PFC polluted sludge was used to prepare the spiked sample because no blank sludge was found. The previous analysis of the sludge showed that it contained very small amounts of PFOS and PFDoA (<LOQ) before spiking, so the PFOS and PFDoA signals were subtracted from the signals obtained for the spiked sample in order to obtain accurate recovery values. Acceptable recovery values higher than 80% were obtained for the PFCs studied (Table 2), except for PFHpA and PFNA (69 and 75%, respectively).

PFCA and PFOS concentrations found by the developed method were compared with those obtained by PLE. Recovery values found with PLE for the spiked sample were between 92±3 and 104±2% for PFOA and PFNA, respectively (shown in Table S5 of supplementary materials). Concentrations found and the *p*-values obtained with the *t*-test used for comparing the results of both methods are shown in Table 3. No significant differences were

Table 1
Study of matrix effect. Comparison of calibration slopes in matrix and standard solution.

	Matrix		Methanolic standard solution	
	Slope ± 95% CI, mL ng^{-1}	R^2	Slope ± 95% CI, mL ng^{-1}	R^2
PFHpA	304.8 ± 10.7	0.9995	254.0 ± 8.12	0.9994
PFOA	368.2 ± 21.2	0.9991	320.8 ± 13.3	0.998
PFNA	509.9 ± 32.1	0.9991	430.3 ± 17.8	0.998
PFOS	478.1 ± 37.1	0.9997	379.0 ± 37.1	0.998
PFDA	608.1 ± 40.8	0.995	452.9 ± 11.2	0.997
PFUnA	635.3 ± 37.2	0.9997	550.1 ± 13.6	0.998
PFDoA	690.4 ± 83.5	0.996	1229.1 ± 111.3	0.993

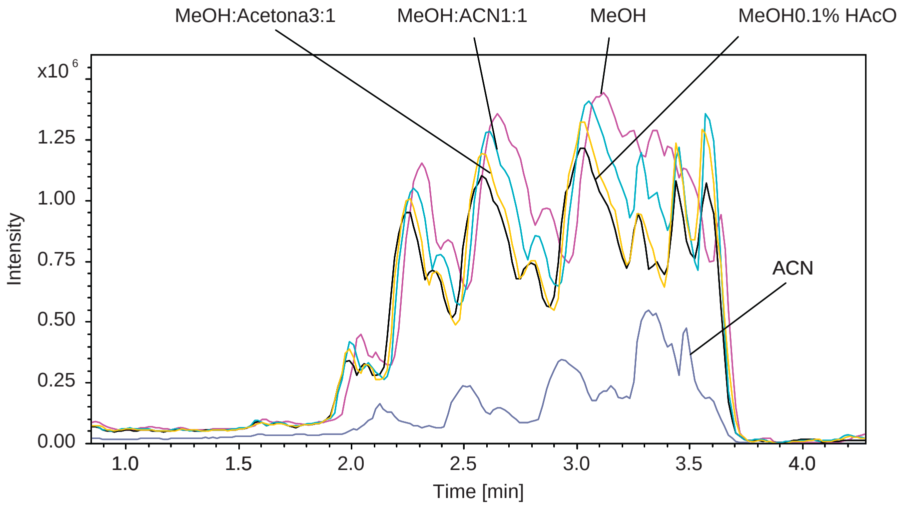

Fig. 3. TIC chromatograms of sewage sludge extracts obtained by FUSLE with different extraction solvents.

found between the results of FUSLE and PLE (p-values > 0.05), except for PFHpA and PFNA, for which lower concentrations were obtained with FUSLE as expected from recovery data.

3.4. Analysis of sewage sludge samples

During the analysis of sewage sludge samples, procedural and instrumental blanks were carried out. Instrumental blanks were performed by injection of methanol in the UPLC–QTOF equipment. No signals were obtain for the analytes in the instrumental blanks. Procedural blanks were performed by processing 8 ml of acetonitrile. They were subjected to FUSLE, evaporation, reconstitution in methanol and UPLC–QTOF analysis. Sometimes very small signal of PFOS were detected in procedural blanks (Fig. 1C). The procedural blank signals were used to determine the LOD values.

Sewage sludge samples were provided by seven different waste water treatment plants of La Rioja. They were treated as described before and analysed following the proposed method. The results of the analysis are shown in Table 3. Low concentration levels were detected. PFOA, with concentration values below 2.82 ng g^{-1} and PFOS, with concentrations from below the LOQ to 3.03 ng g^{-1} were the most commonly analytes found. PFOS was detected in all the samples at low concentrations. Although PFOS levels in sewage sludge are usually high, this is not the first time that low levels are reported; Navarro et al. [7] could detect PFOS only in the 60% of the sewage samples analysed from WWTPs from Spain. This means that there is not important PFCs contamination in the sewage sludge from the studied area (La Rioja), in contrast with the levels found in studies from California, with concentration of PFOS up to 2610 ng g^{-1} [15]; New York, with concentrations from 32 to 346 ng g^{-1} for PFOS and up to 128 ng g^{-1} for PFOA [10] or Catalonia (Spain) with 53–121 ng g^{-1} of PFOS [11]. PFCs concentrations reported in literature are shown in Table 3. In all the studies, the most important contamination comes from PFOS, that was detected in all the analysis with values from below the quantification levels to 2610 ng g^{-1} found in sewage sludges from California in 2005 [15]. Reported PFCs concentrations are also shown in table 4.

Table 2
Features of the FUSLE–LC–MS/MS method.

	LOD[a], ng g^{-1}	LOQ[a], ng g^{-1}	Repeatability[b], %	Intermediate precision[b], %	Recovery[c] ± 95% CI, %
PFHpA	0.10	0.30	4.9	7.4	69 ± 1
PFOA	0.20	0.60	4.3	4.6	83 ± 8
PFNA	0.10	0.30	2.7	7.4	75 ± 6
PFOS	0.10	0.30	0.9	7.1	88 ± 3
PFDA	0.15	0.45	2.2	4.4	92 ± 6
PFUnA	0.07	0.21	2.3	7.3	104 ± 6
PFDoA	0.06	0.18	1.0	6.6	101 ± 6

[a] LOD and LOQ calculated as the concentration that provided a signal-to-noise ratio of 3.3 and 10, respectively.

[b] ANOVA study performed by triplicate during 3 days.

[c] $n=4$.

Table 3
Concentration found in a spiked sample using PLE and FUSLE extractions.

	PLE analysis, ng g^{-1} ± 95% CI	FUSLE analysis, ng g^{-1} ± 95% CI	p-value
PFHpA	15.8 ± 0.4	11.0 ± 0.2	$4.2 \times 10^{-4*}$
PFOA	14.7 ± 0.5	13.4 ± 1.2	0.09
PFNA	16.6 ± 0.4	12.0 ± 1.0	0.006*
PFOS	15.1 ± 0.7	14.2 ± 0.5	0.12
PFDA	13.3 ± 0.1	14.8 ± 1.0	0.06
PFUnA	14.9 ± 0.6	16.8 ± 1.0	0.07
PFDoA	15.5 ± 0.6	16.78 ± 1.0	0.06

* Statistical differences, p-value < 0.05.

4. Conclusions

A fast and simple FUSLE–UPLC–(QTOF)MS/MS method has been developed to determine PFCAs and PFOS in sewage sludge. Extraction variables such as extraction solvent, solvent volume, power and time, were optimised and finally set at 8 mL of acetonitrile at 65% for 20 s; and two extraction steps were shown to provide a complete extraction of the studied PFCs from sewage sludge. The whole method FUSLE–UPLC–MS/MS provided excellent repeatability and intermediate precision, with RSDs below 8% and good recovery values between 69 and 104%. This method provides faster analysis than the other previously reported for the determination of PFCs in sewage sludge, providing an exhaustive extraction in two cycles of 20 s, instead of the two cycles of 15–30 min by USLE reported before [7,15] and avoiding SPE clean-up steps [7,11,15] and consequently saving time and solvents consumption. The FUSLE–UPLC–(QTOF)MS/MS method has been applied to determine PFCAs and PFOS in sewage sludge from different waste water treatment plants of La Rioja. Low concentration levels were found in all the samples.

Table 4
Levels of PFCs found in sewage sludge samples.

	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA	PFDoA
PFC concentrations found in sewage sludge samples from WWTPs of La Rioja by FUSLE–UPLC–MS/MS (ng g^{-1} dry sewage sludge ± 95% CI)							
S1	n.d.	n.d.	n.d.	1.54 ± 0.21	n.d.	n.d.	n.d.
S2	n.d.	0.81 ± 0.05	< 0.30	2.39 ± 0.42	0.88 ± 0.19	n.d.	< 0.18
S3	n.d.	< 0.60	< 0.30	3.03 ± 0.18	1.02 ± 0.29	n.d.	< 0.18
S4	1.84 ± 0.23	2.25 ± 0.43	n.d.	1.38 ± 0.13	n.d.	0.44 ± 0.07	0.35 ± 0.04
S5	0.42 ± 0.09	1.08 ± 0.18	n.d.	< 0.30	n.d.	n.d.	n.d.
S6	< 0.30	2.82 ± 0.39	< 0.30	0.57 ± 0.07	< 0.45	< 0.21	0.48 ± 0.06
S7	< 0.30	2.14 ± 0.43	n.d.	< 0.30	n.d.	n.d.	n.d.
PFC concentrations in sewage sludge reported in literature (ng g^{-1} dry sewage sludge)							
[7]	< 0.01–2	< 0.03–8	< 0.01–10	< 0.01–286.8	< 0.04–24	n.a.	n.a.
[10]	5.4–9.7	8.4–128	4.7–15.2	32.2–346.3	3.4–43.9	4.2–22.8	2.5–19.7
[11]	< LOQ-4.5	9.5–30.3	1.1–2.4	53.0–121.1	6.1–23.5	< LOQ–12.2	2.7–11.3
[15]	n.a.	n.d.-29.4	n.d.-10.3	14.4–2610	< 3–72.5	n.d.-8.58	n.d.-32.7
[16]	n.a.	n.a.	n.a.	35–48	n.a.	n.a.	n.a

n.d.: Non detected, n.a.: non analysed, < LOQ: concentration level lower than the limit of quantification.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.02.020.

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