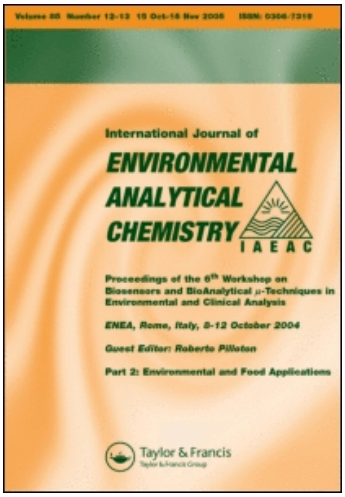

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Application of a new focused microwave technology with species-specific isotope dilution analysis for the quantitative extraction of organometallic contaminants in solid environmental matrices

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A new self-tuning single-mode-focused microwave technology has been evaluated in this work to perform the quantitative routine extraction of organometallic species from solid matrices of environmental interest. Species-specific isotope dilution analysis has been employed to better investigate the real influence of the microwave-assisted extractions on the final results. The advantages of such methodology in comparison with other established microwave units for the routine speciation analysis of organomercury and organotin compounds are discussed (such as the capability of using disposable glass vials, a self-tuning mode to provide an accurate control of the temperature and pressure inside of the vials, and the possibility of performing automated sequence of extractions with low sample size). The results obtained in this work demonstrated that such technology provides a fast and reliable quantitative extraction of the organometallic species in a wide range of extraction conditions even when the multi-elemental (Sn and Hg) species-specific determination is carried out.

Keywords: focused microwave extraction; species-specific isotope dilution; methylmercury; butyltin compounds; solid environmental samples

1. Introduction

Microwaves have been applied in analytical chemistry since 1975 [1] and nowadays are one of the most established sample preparation techniques for a wide range of applications [2]. Besides the minimisation of the analysis time, one of its major advantages is the possibility of homogeneously generating heat inside of the sample, in contrast to the convective heating in which heat is transferred heterogeneously from the source to the walls of the sample containers. The microwave application to the sample can be done using multimode or single mode systems. In the multimode systems, the radiation is dispersed into a relatively large cavity in comparison with the samples leading to a random application of the radiation. On the other hand, the single mode cavities offer highly uniform energy

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distribution and the ability to couple more efficiently with small samples [3,4]. Such focused systems allow a better control of the microwave application to the sample and are extremely useful when extracting from solid samples. Labile compounds and their identity must be preserved throughout the overall procedure [5].

The most illustrative examples of such extractions belong to the field of speciation analysis [6,7]. It is well known that the absorption, metabolism, accumulation and toxicity of a given element depend on its chemical form (species) [8]. Therefore, the need of determining not only the total elemental content but also the different species in which an element is present in a given sample is leading to an increasing number of regulations in national and international policies. One of the most problematic and representative case study is the environmental and toxicological impact of organotin and organomercury compounds [9]. They have been recently included in the list of priority pollutants of the European Union (Decision 2455/2001/EC) and the maximum level of Hg in different foodstuffs has been also regulated to $0.5\,\mu g\,g^{-1}$ (wet weight) (Commission Regulation EC-78/2005). Similar regulations for other matrices such as sediments or foodstuffs are expected in the near future and the development of fast and reliable speciation methodologies able to quantitatively extract these contaminants from solid matrices on a routine basis and without degradation will be demanded worldwide by the analytical laboratories.

In previous works [10,11], it has been demonstrated that the use of species-specific isotope dilution analysis does not provide any enhancement of the extraction recovery. This is explained by the fact that isotope equilibration between the endogenous and the labelled species occurs always on the liquid phase after the release of the endogenous species from the solid matrix. Indeed, after the isotope equilibration is achieved the use of isotope dilution analysis cancels out all the errors involved through the whole procedure except the extraction efficiency. Thus, the use of species-specific isotope dilution analysis appears to be a reliable tool to better evaluate the extraction efficiency of a technique under investigation. The aim of this work is the evaluation and application of a self-tuning single-mode-focused microwave technology to provide reliable routine extraction methodologies for speciation of tin and mercury in solid samples. For this purpose, the individual and simultaneous determination of methylmercury and butyltin compounds in different certified reference materials (CRMs) was carried out. In addition, in order to better evaluate the efficiency of the different extraction conditions assayed, the errors derived from other sample preparation steps were minimised by using species-specific isotope dilution analysis.

2. Experimental

2.1 *Instrumentation*

A focused microwave system Discover (CEM, Matthews, NC, USA) with an autosampler Explorer (CEM) was used to perform the extraction of the organometallic species from the solid samples. When the analysis of the samples was carried out by GC-MS, a Hewlett-Packard (Palo Alto, CA, USA) gas chromatograph Model HP-5890, fitted with a split/splitless injector and a DB-5MS capillary column from Agilent J&W Scientific (cross-linked 5% diphenyl, 95% dimethyl siloxane, $30\,m \times 0.25\,mm$ i.d. $\times 0.25\,\mu m$ coating) was coupled to a Jeol JMS-1000GC (Tokyo, Japan). When the determination of the samples was carried out by GC-ICP-MS, a gas chromatograph, Focus (Thermo Finnigan,

Milan, Italy), equipped with a capillary column Tr-5 from Thermo Finnigan (San Jose, CAL, USA) (cross-linked 5% diphenyl/95% dimethyl siloxane, 30 m × 0.25 mm i.d. × 0.25 μm coating) and an automatic injector was coupled to an X series inductively coupled plasma mass spectrometer (Thermo Electron Corp., Windsford, UK) via the commercially available interface. For the analysis of the BCR-464, an SPME device used for manual extraction, consisting of a holder assembly and a replaceable divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50 μm/30 μm) fibre, was purchased from Supelco (Lyon, France). The fibres were conditioned before use, as recommended by the manufacturer, by heating them in the injection port of the GC for 1 h at 270°C.

2.2 *Reagents and materials*

Methanol, glacial acetic acid, hexane and a 25% (w/v) solution of tetramethylammonium hydroxide was purchased from Sigma-Aldrich (Lyon, France). Tributyltin chloride (95.9%), dibutyltin dichloride (99.9%) and monobutyltin trichloride (99.9%) were obtained from Sigma-Aldrich. A ^{119}Sn-enriched mixture of mono-, di- and tri-butyltin (MBT, DBT and TBT, respectively) was purchased from ISC-Science (Oviedo, Spain), ^{201}Hg-enriched monomethylmercury (MMHg) was synthesised in a previous work from ^{201}Hg-enriched mercury oxide (Oak Ridge National Laboratory). Sodium tetraethylborate (Strem Chemicals, Bischheim, France) was used for the ethylation of the organometallic species. Sodium acetate (99%) was purchased from Sigma-Aldrich and employed to prepare a 0.1 M acetic acid/acetate buffer. The CRMs BCR 710 (oyster tissue) and CRM-477 (mussel tissue) were purchased from the Institute for Reference Materials and Measurements (Geel, Belgium) whereas the CRM SOPH-1 (marine sediment) was purchased from the National Research Council of Canada (Ottawa, ON, Canada).

2.3 *Procedures*

2.3.1 *Extraction of the organometallic species*

A sample weight from 50 to 300 mg of sample was placed inside the microwave glass vessel and spiked with the isotopically labelled compounds according to the random error propagation theory [12]. In this way, the ratio of spiked to sample amount is selected in order to obtain a resulting isotope ratio in the mixture within the interval in which the error in the calculation of the sample concentration is minimum. Immediately, 4 mL of extractant solution, acetic acid: methanol (3 : 1) or TMAH 25% was added. The vial was placed in the focused-microwave autosampler and the extraction was performed in a range from 2 to 6 min and 60–90°C as hold temperature.

2.3.2 *Ethylation, separation and determination by GC-ICP-MS or GC-MS*

Species ethylation was carried out in 7 mL clear glass vials with a screw cap (Supelco, Bellefonte, PA), 300 μL of extract was mixed with 5 mL of acetic acid/acetate buffer 0.1 M at pH 4.9 or 3.9, for butyltins and methylmercury, respectively. The pH of the resulting solution was adjusted with ultra-pure concentrated solutions HCl or NH_4OH. Then, 1 mL of hexane and 0.3 mL of 2% w/v sodium tetraethylborate was added and the vial was shaken manually for 5 min. The organic layer was transferred to a glass vial and the samples were stored at −18°C until analysis. Depending on the concentration in the

organic layer and the detection technique used an additional step of pre-concentration was carried out in a dedicated unit (Evap, Supelco, Bellefonte PA) where the organic layer was pre-concentrated under a gentle stream of nitrogen.

2.3.3 *Analysis of CRMs*

When the analysis of the BCR-464 was carried out, 1 mL of extracted sample diluted in the buffer solution was adjusted to pH 5 and then 1 mL of $NaBEt_4$ (2.5%) was added and the vial was then immediately closed with a PTFE-coated silicon rubber septum. Then the SPME needle was pierced into the septum and the fibre was exposed to the solution headspace for 15 min at room temperature with magnetic stirring. Finally, the fibre was withdrawn into the needle and transferred to the GC injector for thermal desorption for 1 min at 250°C. On the other hand, for the rest of the CRMs analysed in this work by GC-MS, the clean-up of the samples was carried out using Florisil columns as described in a previous publication [13] and transferred to a 2 mL chromatographic vial. In this way, the samples were stored at −18°C and just before the measurement they were pre-concentrated under a gentle stream of nitrogen when necessary.

2.3.4 *Measurement of isotope ratios*

The measurement of the isotope ratios by GC-MS was carried out as reported in a previous publication [14]. Briefly, ^{13}C contributions from the organic groups attached to the tin and mercury atoms were corrected by applying simple mathematical equations. On the other hand, when a GC-ICP-MS was used for the isotope ratios, they were computed as peak area ratios, and the mass bias was corrected by bracketing a natural abundance standard between each triplicate of samples.

3. Results and discussion

3.1 *Self-tuning single-mode microwave cavity*

Closed-vessel microwave systems or focused multimode systems have the unquestionable advantage of processing a variable number of samples at the same time. However, they normally suffer from hot and cold spots inside of the cavities which are problematic when repeatable extraction conditions are needed. In the last years, single-mode cavities with more consistent and predictable energy patterns have become available but they require mechanical tuning devices in the system, when the size or the polarity of the sample varies [3]. As can be observed in Figure 1, the microwave unit employed in this work incorporates a circular cavity and a wave guide that is capable of self-tuning. This type of system features multiple entry points for microwaves into the cavity itself, compensating for variations in the sample characteristics and sample size. The maximum microwave power of the instrument is set in 300 W and a direct pressure control system holding the septum of the extraction glass vial limits the maximum pressure inside of the vessel to 17.3 bar. On the other hand, the temperature control system is based on a non-contact infrared sensor which monitors and controls the temperature conditions of the reaction vessel located in the instrument cavity without introducing a temperature probe inside of the sample. The temperature sensor is centrally located beneath the cavity floor and is set up in a feedback control loop with the magnetron to regulate the power output to maintain the temperature set-point throughout the extraction. These instrumental

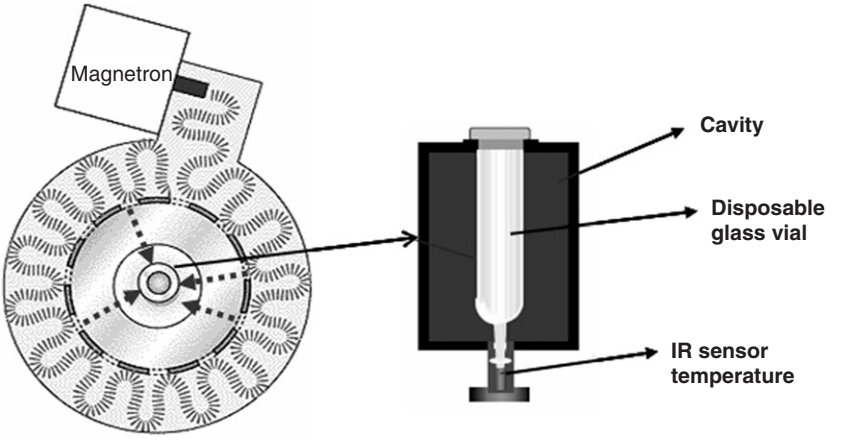

Figure 1. Self-tuning single-mode cavity scheme.

characteristics make the system well suited for solid-liquid extractions of organometallic species at the low nanograms per gram range in which an accurate and reliable control of the extraction conditions must be ensured. In elemental speciation, the identity of the target analytes must be preserved throughout the whole analytical procedure and the optimum extraction conditions must be carried out as repeatable as possible. The external control of the temperature as well as the use of small disposable glass vessels of 10 mL is useful in reducing contamination problems as the use of temperature probes immersed into the sample and the reutilisation of microwave vessels is avoided. Additionally, such reaction vessels allow for work at microscale level performing extractions with minimum sample and solvent size. This facilitates the handling of very limited sample sizes even using analytical balances with precisions of ±0.00001 g. Additionally, working with semi-closed vessels in which the pressure is controlled over the whole extraction procedure permits the analysis of volatile species. Such device allows not only the performance of sequence analysis and hence a more efficient management of time but also the possibility of using specific microwave extraction conditions for different samples. These are an important advantage in comparison with the multimode systems in which the same extraction conditions must be applied for several samples, and the required cleaning of the microwave vessels increases considerably the total sample preparation time.

An example of a solid-liquid extraction with this system is given in Figure 2 where a typical digestion of methylmercury from 0.1 g of tuna fish using 4 mL of TMAH is presented. As can be observed in the temperature profile of the figure, after 1 min of ramp time the programmed temperature of 70°C inside of the vessel was reached and kept constant during 4 min with minimal variations throughout the digestion procedure.

3.2 *Extraction of butyltin compounds and methylmercury from solid samples*

The capabilities of the new microwave technology for the extraction of organometallic species of tin and mercury were evaluated by the analysis of several CRMs. Species-specific isotope dilution analysis was employed in all cases in order to minimise possible sources of

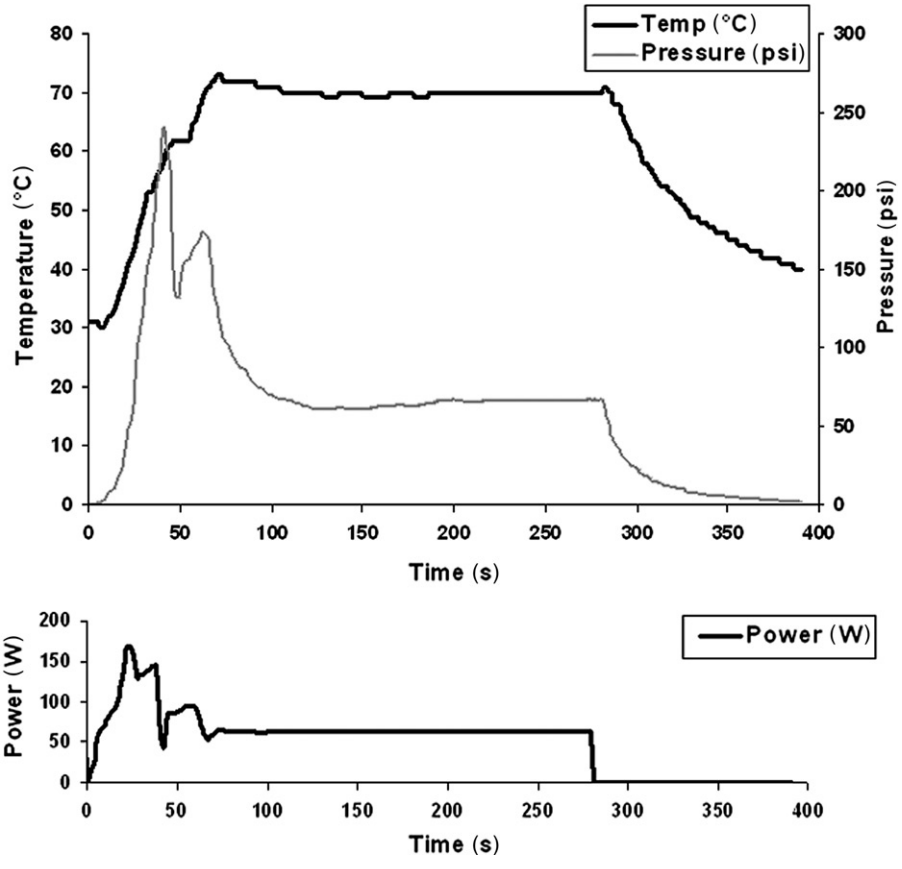

Figure 2. Temperature, pressure and microwave profiles during a methylmercury extraction from tuna fish tissue at 70°C during 4 min using 25% TMAH in water as extractant.

error derived from sample preparation steps different than the microwave-assisted extraction. For this purpose, a commercially available mixture of MBT, DBT and TBT enriched in ^{119}Sn as well as ^{201}Hg-enriched methylmercury (previously synthesised in our laboratory) were used for the experiments. Although the system offers the possibility of fixing the power or the temperature during the extraction, temperature-dependent methods were selected to obtain the most repeatable extraction conditions. It is worth noting that in all cases a maximum ramp time of 60 s was selected to achieve the desired temperature.

On the other hand, although magnetic stirring was employed for the homogenisation of the sample and the extractant during the extraction, the influence of the sample size was investigated due to the narrow geometry of the 10 mL microwave vessels (compared to other vessels commonly used with multimode and single-mode systems). In this sense, as several authors have reported difficulties in the extraction of butyltin compounds, (particularly for MBT) [15,16] different experiments were conducted to find out the influence of the sample size in the extraction efficiency of such species in sediments and biotissues. For this purpose, the extraction of butyltin compounds from the certified sediment SOPH-1 and the mussel tissue CRM-477 at 70°C during 4 min was

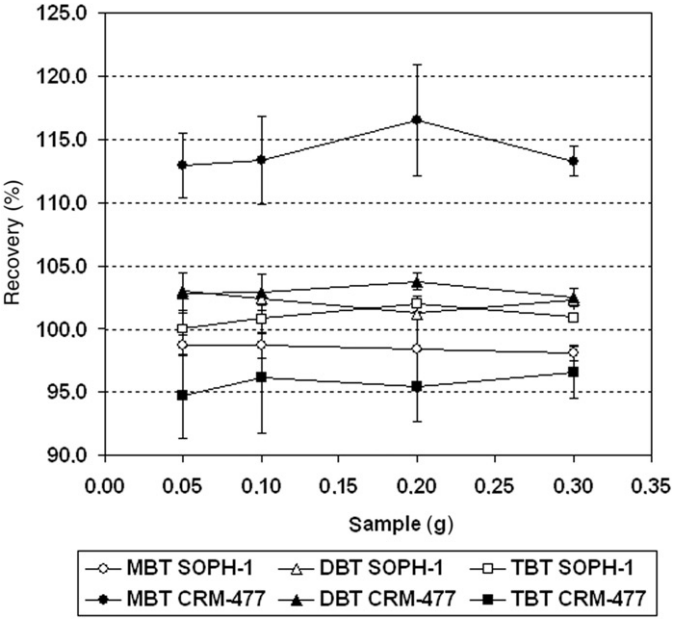

Figure 3. Sample size influence in MBT, DBT and TBT extraction from a certified sediment (SOPH-1) and a certified mussel tissue (CRM-477). MBT recovery in SOPH-1 was obtained using previously published results [16].

carried out using different amounts of sample from 50 to 300 mg and a fixed volume of extractant (4 mL of acetic acid methanol mixture; 3 : 1). Figure 3 shows the recovery from the certified value for each butyltin species and, as can be observed, no significant influence of the sample size is detected when analysing both types of matrices. It is worth noting that although recoveries higher than 100% are systematically obtained for MBT in the CRM-477, these results are in agreement not only with the certified value but also with previous works reporting results on this reference material [11].

The extraction of the tin and mercury species from the CRMs was carried out by using four different temperatures (60, 70, 80 and 90°C) at three different times (2, 4 and 6 min). Table 1 shows the results obtained at different conditions for the five different CRMs analysed: SOPH-1 (marine sediment), CRM-477 (mussel tissue), TORT-2 (lobster hepatopancreas), BCR-464 (tuna fish) and BCR-710 (oyster tissue). It is worth stressing that all the data collected in this table match the certified values for all the species. In the case of butyltin compounds, a complete extraction from the mussel tissue with acetic acid: methanol (3 : 1) was accomplished even at the lower conditions (60°C 2 min^{-1}) obtaining results in agreement with the certified values at almost all conditions with an excellent reproducibility between all the results (3, 1 and 4% for MBT, DBT and TBT, respectively). On the other hand, in the case of the sediment SOPH-1, a higher variability in the results was obtained mainly for MBT in agreement with previous results in this matrix [16]. In addition, any significant increase or decrease in the concentrations of the species with the temperature or time was not observed, ruling out possible degradation or interconversions of the species taking place during the analytical process. As can be observed in Table 1, a quantitative extraction in the entire experimental domain was obtained for DBT and TBT in SOPH-1.

Table 1. Butyltin compounds and/or methylmercury determinations in different certified reference materials at different extractions conditions[a].

Extraction conditions		SOPH-1			CRM-477			TORT-2	BCR-764[b]	BCR-710[b]			
T	Time	MBT	DBT	TBT	MBT	DBT	TBT	MMHg	MMHg	MMHg	MBT	DBT	TBT
60	2	–	–	–	1019	821	853	152	–	–	–	–	–
60	4	123	175	116	990	820	847	155	–	–	–	–	–
60	6	118	169	117	1023	817	828	154	–	–	–	–	–
70	2	–	–	–	1084	809	835	156	–	–	–	–	–
70	4	123	170	119	1051	818	832	151	4967 ± 106	109 ± 4	34 ± 6	49 ± 2	53 ± 3
70	6	117	168	120	1089	807	817	157	–	–	–	–	–
80	2	126	176	117	1080	816	834	145	–	–	–	–	–
80	4	119	170	124	1135	810	815	158	–	–	–	–	–
80	6	132	182	124	1143	793	843	151		–	–	–	–
90	2	133	172	125	–	–	–	–	–	–	–	–	–
90	4	148	169	118	–	–	–	–	–	–	–	–	–
90	6	126	174	134	–	–	–	–	–	–	–	–	–
Average		127	173	121	1069	812	834	153	4967	109	34	49	53
RSD (%)		7	3	5	5	1	2	3	2	4	18	4	6
Certified value		–	174 ± 9	125 ± 7	1013 ± 189	785 ± 61	900 ± 78	152 ± 13	5117 ± 160	107 ± 17	–	–	54 ± 7
Indicative value		–	–	–	–	–	–	–	–	–	34 ± 9	42 ± 9	–

Notes: [a]Concentration expressed as nanograms (Sn or Hg) per gram (dry weight).
[b]Uncertainty expressed as 1 SD of three independent extractions.

In the case of methylmercury, two different matrices were studied: tuna fish and lobster hepatopancreas. In both cases TMAH was employed as extractant instead of acetic acid and methanol. The reference material TORT-2 is certified in MMHg at a level of $152 \pm 13\,ng\,g^{-1}$ and the average obtained from all the experiments was found to be $153 \pm 5\,ng\,g^{-1}$ with a relative SD of 3% between different extraction conditions. Optimum extraction conditions of MMHg were proposed as 70°C for 4 min and were subsequently employed in the extraction of methylmercury in the CRM BCR-464 by SPME-GC-MS. As can be observed in Table 1, results in agreement with the certified value were again obtained with an excellent reproducibility.

Finally, the simultaneous extraction of tin and mercury species was performed by analysing the reference material BCR-710 (an oyster tissue with certified values of methylmercury and TBT and indicative values for MBT and DBT) [17]. Three independent extractions were carried out using TMAH and 70°C during 4 min applying multi-elemental species-specific isotope dilution analysis. The results obtained were not only well in agreement with the certified values of TBT and MMHg but also with the indicative values for MBT and DBT.

4. Conclusions

The application of an innovative self-tuning single-mode microwave technology in the extraction of organometallic species from solid environmental samples allowed the quantitative extraction and determination of monomethylmercury and butyltin compounds in different solid matrices. The use of species-specific isotope dilution analysis in all the experiments allowed us to remove errors derived from other sample preparation steps. It is worth noting that the single isotope spikes employed in this work does not correct for degradation of the species, but the results are in agreement with the certified values which ruled out the occurrence of degradation reaction, at least for the case of butyltin compounds. The results obtained in this work demonstrate that this technology is able to perform the quantitative extraction of these species in a fast, reliable and repeatable routine basis. It is worth noting that the automated extraction of a batch of 10 samples can be performed in less than 1 h which is a shorter total extraction time than when using conventional multimode systems in which the vessels must be previously cleaned.

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