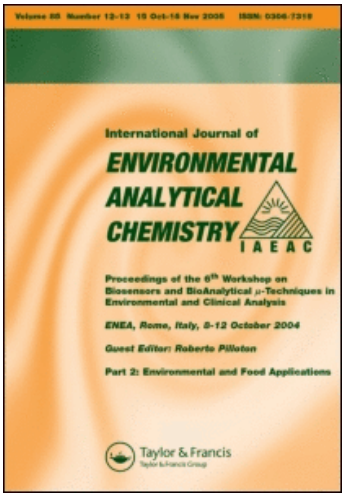

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Microwave-assisted extraction of trichloroethylene from clay samples

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A new method for volatile organic compounds (VOCs) extraction from low-permeability media, such as clay, has been developed and tested using trichloroethylene (TCE) as a model compound. The method is based on microwave-assisted extraction (MAE), which uses microwave energy to heat the extracting solvent and the sample. MAE allows the extraction process to be carried out at elevated temperatures and pressures, which dramatically reduces the time required to complete the process. A custom-made PTFE vessel was used for extraction investigations. TCE analysis was performed using gas chromatography with electron capture detection (GC-ECD). Three different solvents were tested: methanol, 1 : 1 hexane : acetone mixture, and 10 : 1 hexane : acetone mixture. A comparison of TCE recoveries from clay samples using the new method and the standard methanol extraction method was carried out. The newly developed method and the method currently in use were found to recover similar amounts of TCE. The major advantage of the MAE technique is the very short time needed to obtain complete analyte recovery (6–10 min), which makes it possible to analyse a large number of samples without the need for sample preservation or prolonged storage. Thus, the new method is much more efficient than the existing methods. The technique has a good potential for field application.

Keywords: Microwave-assisted extraction; Volatile organic compounds; Trichloroethylene; Clay; Low-permeability media; Soil

1. Introduction

Volatile organic compounds (VOCs) are the most frequently identified constituents in the designation of environmental hazardous waste. Improper disposal of spent chlorinated solvents and leakage of petroleum fuels from underground storage tanks were some of the most important sources of widespread contamination of large areas throughout the world. Many VOCs are mutagens, teratogens and/or carcinogens, and might pose serious health risks [1].

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Numerous industrial sites are contaminated by chlorinated solvents in the subsurface [2]. At many locations, the solvents occur in low-permeability, clayey deposits that can only be practically characterized using cores [3]. The sorption capacity of clay is higher than those of sand or limestone [4]. In order to identify problem areas and efficiently monitor and control them, the assessment of VOC concentration must be performed. This assessment requires that the VOCs be isolated from the matrix before the analysis.

The efficiency of VOC extraction from soils depends on many parameters, including mineralogical composition, particle size, density, and porosity. Sorption capacity of VOCs in soils, which determines the matrix capability to release the compound during extraction, is related mostly to the available surface area [4] and the diffusivity of a contaminant in soil [4, 5], but the water content of the soil, aging, as well as physico-chemical physical properties of the soil might also play an important role [6, 7].

The official US Environmental Protection Agency (EPA) methods for VOC analysis in soils are Method 5035 based on purge and trap, and Method 5021, which uses static headspace analysis [8]. Both methods are not useful for volatile contaminants that have diffused into internal micropores of soil (the usual case for sites that were contaminated for a long time) and/or are strongly sorbed by the matrix [8, 9]. In the investigations reported in this article, soil samples were obtained from a site where the VOC contamination has been in the ground for a few decades, so aging had to be considered an important factor. A standard method used in our laboratory for the determination of chlorinated solvents in such samples, based on methanol extraction of clay subcores, requires 5 days to complete [10].

Several new approaches to the extraction of organic analytes from solid samples have been developed in the last few decades [11–14], including supercritical fluid extraction (SFE), pressurized fluid extraction (PFE) (also called accelerated solvent extraction (ASE)), microwave-assisted extraction (MAE), and sonication extraction [15–17]. Many of these techniques proved to be superior to the traditional Soxhlet extraction in terms of solvent consumption, extraction time, and analyte recovery for soils with high to medium permeabilities [15, 16]. Their usefulness for the determination of VOCs in low-permeability media, including clay, varies depending on the method specifics. A broader discussion of this issue can be found in [18]. In brief, Soxhlet extraction, SFE, and PFE are not suitable for volatile analytes because of the significant potential for losses at the extraction and/or extract recovery stage.

In an earlier contribution [18], we presented a new method for the extraction of chlorinated solvents from clay, based on sonication combined with mechanical agitation. This method allowed complete extraction of the analytes in 0.5–1.5 h, using methanol as the extracting solvent. MAE carried out in sealed, pressure-resistant vessels has the potential to shorten this time even further, as it allows the extraction process to be carried out at elevated temperatures without losses of volatile analytes [19]. The method has been successfully applied for the extraction of selected organic analytes from soils and sediments, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins/furans, phenols, pesticides, and phthalate esters [15, 20–25]. However, to the best of our knowledge, application of this method for the extraction of VOCs from low-permeability media (including clay) has not been reported thus far.

This article reports on the development of a new, fast and simple MAE method for the extraction of chlorinated VOCs from clayey samples. In the study, trichloroethylene

(TCE) was used as the target analyte, as it is one of the most commonly found volatile organochlorine soil pollutants. Method evaluation was based on real contaminated clay samples collected from a former industrial site.

2. Experimental

2.1 *Solvents and standards*

Methanol from Fischer Scientific (Ottawa, ON, Canada), as well as hexane and acetone from Sigma-Aldrich (Oakville, ON, Canada) were used for TCE extraction from natural clay samples. All the solvents were HPLC grade. Hexane was also used as the exchange solvent for GC analysis. Mixtures of 10 and 50% (w/w) acetone in hexane were prepared for TCE extraction. Pure 1,2-dibromoethane (DBE) (Sigma-Aldrich) and pure BDH-assured grade TCE (BDH Inc., Toronto, ON, Canada) were used for standards and solvent preparation. DBE was used as a surrogate standard in methanol and hexane/acetone extractions to compensate for possible analyte losses during sample extraction and assessment of TCE recovery. DBE concentration in methanol was around 38.8 mg L^{-1}; after dilution in the injection solvent (hexane), DBE concentration in the sample injected to the GC was ~510 ppb. DBE concentration in the hexane/acetone mixtures was kept at the same level. Standards of TCE with DBE as the internal standard were prepared at eight concentration levels, from 1 ng mL^{-1} to 3 μg mL^{-1}.

2.2 *Samples*

Native clay samples collected from a former industrial site in Kitchener, Ontario, were used in the study. The samples were contaminated with TCE, which existed in the subsurface for at least 20 years. The core samples were collected from a depth of about 5 m. A detailed description of the site, the samples, and the sampling procedure was presented previously [18]. Clay used in the study was characterized by a relatively high moisture content (3–12%), dry bulk density of 1.96 g cm^{-3}, solid density of 2.88 g cm^{-3}, porosity of 0.3, and fractional organic carbon of 0.24% (dry-weight basis) [18].

2.3 *MAE equipment*

A domestic microwave oven purchased from a local store, Goldstar model no. MS-104YC, was used during method development. The oven had a maximum output of 1100 W at 2450 MHz. In all initial experiments, a custom-built closed vessel (28 mL internal volume) made of PTFE was used to extract TCE from clay samples. The design of the vessel is presented in figure 1. The vessel was tightened with a strap wrench. To prevent catastrophic failure, the thickness of the lid was smaller than the wall thickness. Whenever pressure inside the vessel exceeded a safe level, the lid would lift slightly and allow excess vapours to vent through the hole on the side of the lid. Since this resulted in solvent and analyte loss, care was taken during method development to prevent this from happening by adjusting the solvent volume and/or the irradiation time.

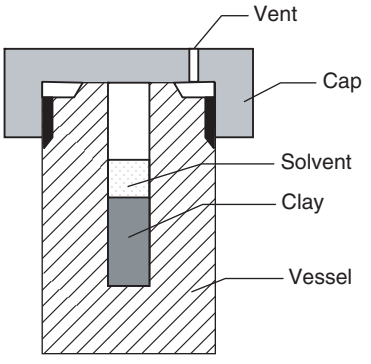

Figure 1. Schematic diagram of the custom-made PTFE vessel for MAE.

No temperature control was used during the extraction. Since only a single extraction vessel was used in the experiments, and the volume of the solvent in the vessel was small, a 400 mL beaker with water was always placed inside the microwave oven to provide an absorber for the microwaves. The external temperature of the vessel immediately after the extraction was measured with a non-contact IR thermometer (Extech Instruments model no. 42529, Waltham, MA). It generally did not exceed 100°C. Before opening, the vessels were cooled in an ice-water bath for ~20 min.

It should be strongly emphasized that due to safety concerns, routine MAE should always be carried out using dedicated systems equipped with temperature and/or pressure control, as well as solvent sensors. The experiments reported in this article were performed using a home-made system because of a lack of access to a commercial instrument at the time. However, such an instrument was purchased immediately after the viability of the method was confirmed. We do not encourage the use of home-made MAE systems. Should there be no other alternative, all precautions must be taken to avoid accidents. In particular, the system should never be run unattended, and the microwave power should be shut off immediately if signs of vessel depressurization are detected.

2.4 *Standard procedure*

The standard procedure for the determination of chlorinated solvents in clay samples used at the Department of Earth Sciences, University of Waterloo, was described in detail in the previous contribution [18]. The method is based on methanolic extraction. In brief, sub-core samples (around 6–10 g) were collected from clay cores and placed immediately in 25 mL vials with screw caps and Tegrabond septa containing 20 mL of methanol. Each vial was then agitated vigorously for 1 min using a standard Mini-vortex stirrer (VWR International, Mississauga, ON, Canada), and for another 30 min on an orbital shaker model 3520 (Lab-Line Instruments, Inc., Melrose Park, IL) at 300 rpm. Samples prepared in this way were allowed to equilibrate for 5 days, following which they were centrifuged for 30 min with a CRU-5000 centrifuge (Damon/IEC, Needham Heights, MA) at 1700–1800 rpm. Samples for final analysis by

gas chromatography (GC) were prepared by dissolving 20 μL of the MeOH extract in 1.5 mL of hexane containing DBE as the internal standard.

2.5 *Method evaluation*

Two methods were used to evaluate the performance of MAE on real clay samples. In the first method, aliquots of the extracts of clay samples processed by MAE were analysed immediately after the extraction and after 5 days of equilibration with the solvent, as in the standard procedure. Complete analyte recovery was assumed when the concentration of TCE in the extract did not change after the additional equilibration time.

In the second method, clay subcores (about 3 cm in length and 1.5 cm in diameter) were cut into slices 3–5 mm thick. Each slice was then cut into four parts. Two opposite quarters were transferred to the extraction vessel and subjected to the MAE procedure. The other two quarters were processed using the standard procedure. In both cases, the volume of the solvent used was adjusted to the small mass of the sample. Care was taken to finish the entire slicing and quartering process in as short a time as possible, to avoid significant analyte losses. The TCE concentration in clay determined by the two methods was then compared.

2.6 *GC method*

Analyses were performed on an HP6890 GC (Agilent Technologies, Mississauga, ON, Canada) equipped with a μ-ECD detector and a capillary fused silica column, 30 m × 0.530 mm × 3.0 μm DB-624 (J&W Scientific, Folsom, CA). The carrier gas, helium (Ultra High Purity, Praxair, Mississauga, ON, Canada), was set to a constant flow rate of 8.1 mL min^{-1}. Injection was performed in pulsed splitless mode. A 1 μL aliquot of the liquid sample was injected using the autosampler. The injector temperature was set to 225°C. The column was kept for 3 min at 55°C, followed by an increase to 105°C at a rate of 30°C min^{-1}. The column was held at this temperature for a further 2 min. The detector was operated at 300°C using nitrogen (ECD grade, Praxair) as the makeup gas at a flow rate of 60 mL min^{-1}.

3. Results and discussion

The standard method for VOC extraction from clay samples currently in use at the Department of Earth Sciences, University of Waterloo, requires the samples to equilibrate with the solvent for 5 days before steady-state concentration of the analyte in the extract is reached. This long period of time makes field analysis impractical and creates the potential for increased analyte losses and cross-contamination. On-site analysis yields results immediately, supporting real-time decisions when delineating limits of contamination during site characterization or soil remediation. In a previous article [18], we presented the development of a new method for VOC evaluation in low-permeability media, namely the sonication-extraction combined with mechanical agitation. The new method produced results comparable with the standard method

but required only 0.5–1.5 h to complete the extraction. As a continuation of this study, we looked for methods that would allow the extraction time to be shortened even further. Another goal was to increase the method sensitivity by eliminating the need for solvent exchange before the analysis [18].

A number of enhanced extraction techniques were considered. ASE seemed an attractive alternative, as it allows the extraction to be carried out at an elevated temperature and pressure. However, preliminary experiments revealed that the technique in its commercial implementation is not well suited for the extraction of volatile compounds. The main reason for this seems to be the fact that the solvent expelled from the extraction vessel to the collection vial is hot, which leads to volatile analyte losses and irreproducible results.

In light of these findings, MAE was selected as the most promising alternative. Similarly to ASE, MAE allows the extraction to be carried out at elevated temperature and pressure, but losses of volatile analytes can be easily prevented if the extraction vessel is allowed to cool down before opening. Extraction times with MAE reported for different applications are typically very short (usually less than 10 min) [15].

Parameters that might affect the efficiency of MAE include the type of solvent, temperature, pressure, extraction time, soil type, and water content [15, 16, 26]. Among these factors, solvent selection plays an important role. The microwave absorbing properties of the solvent, the interaction between the matrix and the solvent, and analyte solubility in the solvent, should all be considered in order to optimize the extraction process [12]. Improved extraction efficiencies in MAE are the result of the high temperature of extraction, since the diffusivity of the analyte and the solvent, as well as the rate and extent of desorption, increase with temperature [15].

The nature of the matrix in which the analytes are bound has a significant effect on the recovery. Spiked samples yield higher recoveries than natural samples in most of cases. This can be explained by the effect of aging on analyte recoveries. Native analytes are more strongly attached to the sample matrix than spiked analytes. They also penetrate deeper into the pores of the matrix [15]. In our previous contribution [18], we have reported on unsuccessful attempts at producing spiked clay samples that would behave similarly to real contaminated samples, exposed to the contaminant for several decades. Due to this, the method evaluation was carried out exclusively using real contaminated samples from a former industrial site in Kitchener, Ontario (Canada). The difficulty with this approach is that because of the inhomogeneity of analyte distribution in clay, it is virtually impossible to collect two subcore samples with the same TCE concentration for comparison purposes. Dense non-aqueous phase liquids, including TCE, spread through the matrix primarily along fractures. Provided there is enough time, they also diffuse into the micropores of the matrix [27]. As a result, the distribution of the contaminant is very non-uniform, with high concentrations near the fractures and much lower concentrations further away.

To overcome this problem, two methods were chosen for the evaluation of MAE efficiency. In the first method, clay samples were subjected to MAE, and aliquots of the extracts were analysed immediately after opening the vessel. Following the aliquot collection, the contents of the MAE vessel were transferred to a 25 mL screw-top glass vial, and the vessel was rinsed with fresh solvent, which was then combined with the extract in the vial. The exact amount of solvent added was determined by weighing the vial before and after each step. Samples prepared in this way were then allowed to equilibrate with the solvent for 5 days, which was shown to be sufficient to recover the

analyte in the standard procedure. After the equilibration, another aliquot of the extract was taken and analysed. TCE concentration in this extract was adjusted for the dilution resulting from the solvent rinse during sample transfer from the MAE vessel to the glass vial. It was assumed that quantitative analyte recovery was achieved in MAE if the concentration of the analyte in the extract did not increase significantly after the 5 day equilibration.

To confirm that analyte recovery in MAE was at least comparable with that in the standard procedure when hexane/acetone mixtures were used for the extraction, a second method was also applied. Since it could not be reasonably assumed that TCE concentration in any two subcores was identical, single subcores were sliced and quartered (see section 2). Portions of the same slice were then analysed by MAE and by the standard method. Solvent volumes were adjusted to account for the smaller amount of the sample. For the final comparison, TCE concentration in clay was calculated for each method. The two methods were considered equivalent in terms of analyte recovery if the concentrations determined for a given slice did not differ significantly.

Initial experiments were performed with methanol as the extracting solvent. Methanol is polar and as such absorbs microwave radiation strongly. It is water-miscible, so it wets the samples efficiently and penetrates the pores easily. The standard procedure is based on methanol extraction, which was shown to be the most efficient method of VOC extraction from soils [8]. Extraction times of 2–8 min were investigated, and it was found that for a vast majority of the samples, 4 min was sufficient to obtain complete recovery of the analyte; however, the optimum extraction time was set at 6 min for clay samples, with masses ranging from 0.5 to 1.2 g to maintain a safety margin. Solvent volumes of 2, 3, and 5 mL were used in the optimization process, and the optimal volume was found to be 3 mL. Larger volumes led to unnecessary extract dilution, which degraded the sensitivity of the method.

Table 1 summarizes the results obtained for 19 clay samples extracted under optimized conditions (6 min microwave extraction time, 3 mL of methanol). The analyte concentration in the extract immediately after MAE was compared with the concentration after an additional 5 days of equilibration with the solvent. The comparison was made using Student's t test for the individual differences [28]. The null hypothesis was that the two methods produced identical results, and the differences were caused by random factors only. The alternative hypothesis was that the differences were caused by systematic factors. Details of the procedure were described in the earlier contribution [18].

Since analyte levels in the samples examined varied widely, we compared the percentage relative differences rather than absolute differences. The average difference between analyte concentrations after 5 days and immediately after MAE had a negative sign, so we compared the absolute value of the calculated test statistic t with the critical value of t at the 95% probability level. This was in essence equivalent to calculating the value of t for the difference between the results obtained immediately after MAE and after 5 days of equilibration. We found that the absolute calculated t value was higher than the tabulated t value; therefore, we had to conclude that the two sets of results differed significantly. A small, but statistically significant decrease in concentration was observed for nearly all samples after they were equilibrated for 5 days. This phenomenon indicates that complete or near-complete analyte recovery was achieved by MAE, and the subsequent decrease in analyte concentration was caused by losses during storage (e.g. through sorption). According to the results presented in table 1,

Table 1. TCE concentration in clay extracts using methanol as the extracting solvent. Solvent volume 3 mL, extraction time 6 min.

Sample	TCE conc. after MAE ($ng\,mL^{-1}$)	TCE conc. after 5 equilibration days ($ng\,mL^{-1}$)	Difference ($ng\,mL^{-1}$)	Relative difference (%)	Average relative difference (%)	Std. dev.	Calculated Student's *t*	Critical Student's *t* (95% confidence level)
1	133	137	4	2.92				
2	36	37	1	2.70				
3	71	70	−1	−1.43				
4	47	45	−2	−4.44				
5	21	20	−1	−5.00				
6	60	60	0	0.00				
7	57	57	0	0.00				
8	47	48	1	2.08				
9	49	49	0	0.00	−1.88	3.03	2.698	2.095
10	51	51	0	0.00				
11	45	44	−1	−2.27				
12	51	50	−1	−2.00				
13	61	61	0	0.00				
14	32	30	−2	−6.67				
15	39	37	−2	−5.41				
16	58	56	−2	−3.57				
17	36	34	−2	−5.88				
18	36	34	−2	−5.88				
19	124	123	−1	−0.81				

the confidence interval for the percentage relative difference between the two sets of results at the probability level of 95% was $-1.88\% \pm 1.36\%$.

While the method developed accomplished complete analyte recovery in a very short time, solvent exchange was still required as in the standard procedure because of the incompatibility of methanol with the stationary phase used in GC analysis. This resulted in reduced method sensitivity. To overcome this problem, alternative, less polar solvents were examined. Hexane is an excellent injection solvent, but it is transparent to microwaves and does not heat up when exposed to microwave radiation. Rapid extraction of VOCs from soil samples immersed in hexane and exposed to microwaves is theoretically possible, as long as the samples contain enough moisture. Under such circumstances, water in the samples heats up and drives the analyte out of the matrix and into the solvent. However, preliminary experiments indicated that the results obtained by such a method were poorly reproducible, mostly because of the varying water content of the samples. To overcome this problem, hexane : acetone mixtures were used in further experiments. Acetone is miscible with both water and hexane. It is also an efficient microwave absorber, so it heats up when exposed to microwave radiation. Two hexane : acetone mixtures were used in the experiments, 1 : 1 and 10 : 1 (w/w).

Method development was conducted as before. Different volumes of both hexane : acetone mixtures (2–5 mL) and various extraction times (6–12 min) were examined. Once the optimal conditions were determined, the performance of the method was evaluated using both methods described above (comparison of analyte concentration immediately after the extraction with the concentration after 5 days, and

Table 2. TCE concentration in clay extracts for 2 mL mixture of 1 : 1 (w/w) hexane : acetone and 10 min extraction time.

Sample	TCE conc. after MAE ($ng\,mL^{-1}$)	TCE conc. after 5 equilibration days ($ng\,mL^{-1}$)	Difference ($ng\,mL^{-1}$)	Relative difference (%)	Average relative difference (%)	Std. dev.	Calculated Student's *t*	Critical Student's *t* (95% confidence level)
1	206	209	3	1.44				
2	182	183	1	0.55				
3	154	153	−1	−0.63				
4	274	270	−4	−1.48				
5	218	223	5	2.24	0.65	1.09	1.896	2.228
6	227	230	3	1.30				
7	340	341	1	0.29				
8	212	215	3	1.40				
9	217	219	2	0.91				
10	194	195	1	0.51				

Table 3. TCE concentration in clay extracts for 2 mL mixture of 10 : 1 (w/w) hexane : acetone and 10 min extraction time.

Sample	TCE conc. after MAE ($ng\,mL^{-1}$)	TCE conc. after 5 equilibration days ($ng\,mL^{-1}$)	Difference ($ng\,mL^{-1}$)	Relative difference (%)	Average relative difference (%)	Std. dev.	Calculated Student's *t*	Critical Student's *t* (95% confidence level)
1	161	158	−3	−1.90				
2	132	133	1	0.75				
3	104	105	1	0.95				
4	151	150	−1	−0.67				
5	87	88	1	1.14	0.87	1.54	1.783	2.228
6	96	98	2	2.04				
7	115	117	2	1.71				
8	115	118	3	2.54				
9	141	140	−1	−0.71				
10	69	71	2	2.82				

comparison of the results obtained by MAE with the results obtained by the standard method for quartered samples).

Tables 2 and 3 present a comparison of the results obtained immediately after the MAE procedure with the results obtained for the same samples after they were equilibrated for an additional 5 days with the two extracting solvent mixtures, 1 : 1 and 10 : 1 hexane : acetone. According to these tables, when an extraction time of 10 min and 2 mL of solvent mixture were used, no significant change in the TCE concentration in the extract occurred after the additional equilibration time. Student's *t* test was applied similarly as in MAE with methanol to examine the data. The calculated values of Student's *t* were 1.896 and 1.783, respectively. Both values were smaller than the critical value of *t* at the 95% probability level, equal to 2.228 for the 10 investigated

samples. The confidence intervals of the average percent relative differences at the 95% probability level for the two investigated mixtures were 0.65 ± 0.67 and 0.87 ± 0.95, respectively. Thus, in both cases, the analyte concentration after 5 days of equilibration with the solvent mixture was not statistically different from the concentration immediately after MAE, which was a strong indication that the analyte was recovered quantitatively from the samples in the MAE procedure.

Tables 4 and 5 present a comparison of the results of TCE determination in clay samples by MAE using the two solvent mixtures with the results obtained for the corresponding quartered samples by the standard procedure based on methanol extraction. The average ratio of the results obtained by the two methods was 0.97 for the 1 : 1 hexane : acetone mixture, and 1.02 for the 10 : 1 mixture, with standard deviation values of 0.04 and 0.14, respectively. The confidence intervals of the average differences were 0.97 ± 0.03 and 1.02 ± 0.10. Thus, an excellent agreement was obtained between the new method and the standard method for both solvent mixtures, even though potentially the samples originating from the same quartered slices could have been not identical.

Both mixtures, 1 : 1 and 10 : 1 hexane : acetone, could be injected into the GC in splitless mode without the need for solvent exchange. Thus, the 76-fold dilution of the extracts required in the standard method was avoided, and the sensitivity of the method was correspondingly improved by the same factor. The estimated limit of detection for TCE in the extracts was $0.1\,\mu g\,L^{-1}$. The limits of detection for the clay samples depended on the mass of the sample taken for the extraction and the amount of solvent used for the extraction and transfer of the sample. For a 1 g sample, the estimated limit of detection was $\sim 0.6\,\mu g\,kg^{-1}$ for both mixtures, and the limit of quantitation was $\sim 2\,\mu g\,g^{-1}$.

4. Conclusions

Compared with the standard method, the time required to complete the extraction with the MAE method was reduced from 5 days to a maximum of 10 min. This was also shorter than the time required for the sonication/agitation method developed previously [18]. In addition, the need for solvent exchange was eliminated when the hexane/acetone mixtures were used. Since several samples can be processed by MAE simultaneously (provided that more vessels are available), it is possible to analyse a large number of samples in a short time, without the need for sample preservation and prolonged storage. Consequently, the method developed can be easily adopted for the needs of field analysis, where immediate results support real-time decisions regarding limits of contamination during site characterization and remediation activities.

In the study, a custom-made apparatus was used. However, the use of a dedicated commercial microwave extraction system is strongly recommended because of better control of the experimental parameters and safety concerns. In fact, once the viability of the method was demonstrated, we purchased a commercial system equipped with high pressure vessels and temperature control.

Table 4. Comparison of TCE concentrations in clay determined using MAE with 1 : 1 hexane : acetone mixture (2 mL, 10 min extraction time) and the standard methanol extraction for quartered clay slices.

Sample	Solvent	Sample mass (g)	TCE conc. in the extract after MAE (ng mL^{-1})	TCE conc. in the extract after 5 days (ng mL^{-1})	TCE conc. increase after 5 days (%)	TCE conc. in methanol extract after 5 days by std. method (ng mL^{-1})	TCE conc. in clay (ng g^{-1})	Conc. by MAE/conc. by the stand. method	Ave.	Std. dev.
1	Hex./acet.	0.4456	206	209	1.44		925	0.94		
1a	Methanol	0.5778				284	983			
2	Hex./acet.	0.4013	182	183	0.55		907	0.91		
2a	Methanol	0.4608				230	998			
3	Hex./acet.	0.3357	154	153	−0.65		917	1.02		
3a	Methanol	0.3217				144	895			
4	Hex./acet.	0.7614	274	270	−1.48		720	0.95		
4a	Methanol	0.5693				215	755			
5	Hex./acet.	0.4523	218	223	2.24		964	0.93		
5a	Methanol	0.4616				239	1036		0.97	0.04
6	Hex./acet.	0.6327	227	230	1.30		718	0.95		
6a	Methanol	0.5834				221	758			
7	Hex./acet.	0.7510	340	341	0.29		905	1.04		
7a	Methanol	0.5414				235	868			
8	Hex./acet.	0.6616	212	215	1.40		641	0.98		
8a	Methanol	0.6487				212	654			
9	Methanol	0.6853	217	219	0.91		633	0.99		
9a	Hex./acet.	0.6537				210	642			
10	Methanol	0.5994	194	195	0.51		647	0.94		
10a	Hex./acet.	0.6240				215	689			

Table 5. Comparison of TCE concentrations in clay determined using MAE with 10:1 hexane:acetone mixture (2 mL, 10 min extraction time) and the standard methanol extraction for quartered clay slices.

Sample	Solvent	Sample mass (g)	TCE conc. in the extract after MAE ($ng\,mL^{-1}$)	TCE conc. in the extract after 5 days ($ng\,mL^{-1}$)	TCE conc. increase after 5 days (%)	TCE conc. in methanol extract after 5 days by std. method ($ng\,mL^{-1}$)	TCE conc. in clay ($ng\,g^{-1}$)	Conc. by MAE/conc. by the stand. method	Ave.	Std. dev.
1	Hex./acet.	0.5058	161	158	−1.90		637	0.99		
1a	Methanol	0.4823				155	643			
2	Hex./acet.	0.4872	132	133	0.75		542	0.97		
2a	Methanol	0.5002				139	556			
3	Hex./acet.	0.4187	104	105	0.95		497	0.96		
3a	Methanol	0.3881				100	515			
4	Hex./acet.	0.5396	151	150	-0.67		560	1.00		
4a	Methanol	0.5944				166	559			
5	Hex./acet.	0.4247	87	88	1.14		410	1.15		
5a	Methanol	0.4543				81	357		1.02	0.14
6	Hex./acet.	0.3888	96	98	2.04		494	1.32		
6a	Methanol	0.4154				77.5	373			
7	Hex./acet.	0.4923	115	117	1.71		467	1.08		
7a	Methanol	0.5004				108	432			
8	Hex./acet.	0.6002	115	118	2.54		383	0.82		
8a	Methanol	0.5378				125	465			
9	Methanol	0.5845	141	140	−0.71		482	1.00		
9a	Hex./acet.	0.4960				120	484			
10	Methanol	0.3338	69	71	2.82		413	0.87		
10a	Hex./acet.	0.3363				80	476			

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