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Headspace single drop microextraction of methylcyclopentadienyl-manganese tricarbonyl from water samples followed by gas chromatography–mass spectrometry

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Abstract

Headspace single drop microextraction coupled to gas chromatography–mass spectrometry yielded a simple, fast and virtually solventless analytical protocol used for the headspace analysis of aqueous samples contaminated with methylcyclopentadienyl-manganese tricarbonyl (MMT). Initially, several experimental parameters were controlled and optimized and the optimum conditions found were 2.5 μl octane microdrop exposed for 20 min to the headspace of a 10 ml aqueous sample (15 ml vial) containing 20% (w/v) NaCl and stirred at 1250 rpm. The calculated calibration curves gave a high level of linearity for MMT with correlation coefficients >0.9995 after conducting a 3-day study. The limit of detection was calculated to be 0.21 $\mu g\,l^{-1}$. The proposed method achieved an enrichment factor of the order of 2100 and a 53% recovery after extracting the spiked aqueous solution for 20 min under the optimized experimental conditions. The repeatability and intra-day reproducibility of the proposed method, expressed as relative standard deviation were 8.4 and 6.4%, respectively. Finally, analysis of spiked tap and wastewater samples revealed that matrix had little effect upon extraction.

Keywords: Headspace SDME; MMT; GC–MS; Liquid-phase microextraction

1. Introduction

There is increased concern within the scientific community concerning the neurotoxicity of manganese, owing part to the use of methylcyclopentadienyl-manganese tricarbonyl (MMT) as a gasoline fuel additive [1]. Indeed, MMT is highly toxic to some animals through inhalation, ingestion and skin absorption [1,2]. Although MMT is known to photolyze rapidly under sunlight, it is fairly stable in the absence of light with half-lives ranging from 0.2 to 1.5 years in aquifer materials at 25 °C [3].

Today, different analytical protocols are available for the determination of MMT in air, water and gasoline samples. These methods mainly use gas chromatography (GC) coupled to a variety of detectors, such as atmospheric pressure helium microwave plasma emission system [4], direct current argon plasma emission [5], atomic absorption in a slotted quartz tube [6] and electron-capture detection [7]. The use of a high performance liquid chromatography system coupled with a laser-excited atomic fluorescence spectrometric detector [8] has also been reported. Recently, the use of solid phase microextraction (SPME) followed by gas chromatography and plasma atomic emission detection [9] or direct thermal desorption and detection by quartz furnace-atomic absorption spectrometry [10] has been proposed for the determination of MMT in water and gasoline samples following another publication dealing with the SPME analysis of MMT in beverages using SPME and gas chromatography coupled to atomic absorption spectrometry [11].

The inorganic applications of single drop microextraction (SDME) for sample preparation appeared in 2003 [12], following the inception of this technology in 1996 [13]. The limited numbers of reports dealing with these applications use a microliter drop of the extractant acceptor phase directly exposed to

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the aqueous donor solution or to the headspace above it and represent an emerging field of study due to the inherent advantages of being fast, inexpensive, precise and virtually solventless. To date published methods were capable of determining trace levels of arsenic [12], arsine [14], organotin [15], methylmercury [16], selenium [17,18], organotin and organomercury [19], cadmium and lead [20], aluminium [21] or a mixture of metals [22] in environmental and biological matrices.

The objective of this work was to investigate the applicability of headspace SDME followed by GC with mass spectrometry used for the determination of MMT in water samples. Experimental parameters affecting the extraction process of MMT (namely organic solvent, organic drop volume, sample stirring, salt addition and sampling time) were controlled and optimized and the performance of the proposed method was evaluated. The developed method was applied to tap and wastewater samples in order to assess the effect of matrix upon extraction.

2. Experimental

2.1. Chemicals and aqueous samples

Methylcyclopentadienyl-manganese tricarbonyl (MMT) was purchased from Aldrich (Milwaukee, WI, USA), 1-octanol and methanol were purchased from Riedel-de Haën (Seelze, Germany) and *n*-octane (≥99% pure) was purchased from Flucka (Steinheim, Switzerland). Deionized water was prepared on a water purification system (EASYpure® RF) supplied by Barnstead/Thermolyne Corporation (Dubuque, IO, USA). Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples.

A 1000 mg l^{-1} of MMT in methanol was prepared and was used as a standard stock solution. From this a 10 mg l^{-1} of MMT in methanol was prepared each week and was used for the preparation of aqueous spiked solutions at the concentration levels of interest. All MMT methanolic solutions were stored at 4 °C in the dark. Recovery studies were carried out using tap and wastewater samples taken from a car wash unit situated in a local petrol station (Chania, Greece). Samples were collected in 250 ml pyrex borosilicate amber glass containers with caps, lined with aluminium foil. They were stored in the dark at 4 °C and were analyzed within 24 h of collection. Before extraction, samples were centrifuged in order to remove any solid particles and the ionic strength of the water samples was then adjusted to the one required by the extraction method used. Preliminary analyses of both samples under the full-scan and selective ion monitoring (SIM) mass spectrometry modes ensured that they were free of the target analyte.

2.2. Headspace SDME

For headspace SDME, 10 ml of a salted (20%, w/v, NaCl) aqueous solution spiked at a known concentration with MMT, was placed in a 15 ml crimp top glass vial covered with aluminium foil containing a PTFE-coated stirring bar and fitted with a Mininert valve (Supelco, Bellefonte, PA, USA). Aqueous spiked samples were freshly prepared, in order to eliminate volatilization losses. In addition, before extraction each sample destined for analysis was stirred at the stirrer's maximum steering speed, allowing thus equilibrium to be attained between the aqueous and gaseous phases.

A 10 μl Hamilton Gastight syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland), Model 1701, with a bevel needle tip (length: 5.1 cm, i.d.: 0.013 cm, bevel 22°), typically containing 2.5 μl of the appropriate organic solvent was clamped above the vial containing the water sample. For all quantification experiments, 2.5 μl of *n*-octane solution was used. The microsyringe was then lowered and its needle passed through the Mininert valve until the tip of the needle was 1 cm below the lower surface of valve. The plunger was depressed and the 2.5-μl drop of the organic phase was exposed to the headspace above the sample. The analytes were then allowed to partition between the headspace and the organic phase at room temperature for 20 min (unless otherwise stated within the text). After extraction, the microdrop was retracted into the microsyringe and transferred to the heated injection port of the gas chromatograph–mass spectrometer (GC–MS) for analysis.

2.3. GC–MS analysis

All analyses were carried-out on a Shimadzu GC-17A, Version 3, QP-5050A Gas Chromatograph/Mass Spectrometer system (Shimadzu Corporation, Kyoto, Japan) equipped with a 30 m × 0.25 mm × 0.25 μm HP-5MS capillary column (Agilent Technologies). The injector was maintained at 250 °C and operated in the splitless mode with the split closed for 5 min. Helium (>99.999% pure) was used as the carrier gas at a flow-rate of 1.2 ml min^{-1}. The column oven was initially set at 50 °C for 2 min, programmed to 250 °C at a 20 °C min^{-1} rate, where it was held for 1 min. The interface temperature was set at 290 °C and the detector voltage at 1.50 kV. A 7 min solvent cut time was allowed for all analyses. The ionization mode was electron impact (70 eV). A SIM program was constructed for GC–MS acquisition and quantification. The latter was based on the target ion (*m/z*) 218. Prior to quantification in the SIM mode, the full scan mode (*m/z* 40–350) was used for identification of target compound based on their mass spectra and GC retention time. The enrichment factor and extraction recovery were determined by comparing the peak area obtained after extracting with the proposed method a 1 μg l^{-1} aqueous MMT solution, with the one obtained by direct injection of the same solvent volume of a 1 mg l^{-1} hexane solution of MMT.

3. Results and discussion

3.1. Optimization of headspace SDME

Initially, a step-by-step optimization scheme has been adopted and parameters, such as organic solvent, sample volume, organic drop volume, stirring rate, salt effect and sampling time were controlled and optimized.

Two solvents (namely octane and 1-octanol) were initially tested and used for extracting the target analyte. Solvent selectivity was evaluated after exposing for 5 min a 3 μl organic solvent

drop to the headspace of a 15 ml glass vial containing 5 ml deionized water samples, stirred at 1000 rpm and spiked at 100 μg l^{-1} with MMT. Both examined solvents had a low volatility restricting thus solvent evaporation during extraction. However, elution of 1-octanol was found to interfere with the target eluting analyte. Octane on the other hand provided a high solubility for MMT and exhibited an excellent chromatographic behaviour. Accordingly, it was decided to use octane as the extraction solvent for all subsequent experiments.

In general, during headspace SDME, increasing the sample volume and consequently decreasing the headspace volume when the same type of vial is used, enhances the extraction of target analytes and improves the sensitivity of the method [23]. Accordingly, in the present studies, the headspace of 15-ml vials containing sample volumes of 5, 7 and 10 ml, stirred at 1000 rpm and spiked at 100 μg l^{-1} with MMT, was extracted with 3 μl of octane for 5 min. As expected the results revealed that extraction is optimized for 10 ml sample volumes.

Although, the use of larger drops is expected to result in an increase of the analytical response of the instrument, their use has been reported as less reliable and more difficult to manipulate [24]. In a separate set of experiments the effect of drop volume upon extraction was investigated. The headspace of 10 ml sample volumes contained in 15 ml vials spiked at 100 μg l^{-1} MMT stirred at 1000 rpm was extracted for 5 min using octane drop volumes ranging from 1.5 to 3 μl. As can be seen in Fig. 1, increasing the organic drop volume from 1.5 to 2.5 μl, resulted in a small increase of the extraction efficiency. However, a further increase of the octane drop from 2.5 to 3 μl resulted in a decrease of the extraction efficiency. This observation is in agreement with previous published reports dealing with the headspace SDME extraction of analytes present in water samples [23,25]. Accordingly, it was decided to use a 2.5 μl octane drop for all subsequent experiments.

Next, the effect of sample agitation upon extraction was investigated. It has been repeatedly reported that sample agitation enhances extraction and reduces the time to thermodynamic equilibrium [24]. For the purpose of the present investigations, 2.5 μl octane drops were exposed each time for 5 min to the headspace of 10 ml water samples spiked at 100 μg l^{-1} with MMT and stirred at different agitation rates (namely: 0, 400, 700, 1000 and 1250 rpm). As expected, the results revealed that agitation dramatically enhanced extraction reaching a maximum at 1250 rpm (Fig. 2). Based on the above observations 1250 rpm was selected as the optimum agitation rate.

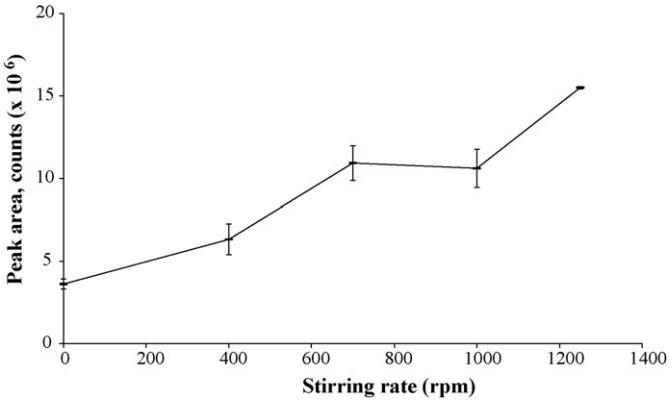

Fig. 2. Effect of sample agitation on the extraction efficiency of headspace SDME used for the analysis of MMT in water samples. Other experimental conditions: 100 μg l^{-1} concentration level; 10 ml sample volume in 15 ml glass vial; 2.5 μl octane drop; 5 min sampling time.

Addition of salt to the sample and accordingly increasing the ionic strength of the aqueous solution may have several effects on extraction. Depending on the solubility of the target analytes, extraction is usually enhanced with increased salt concentration and increased polarity of the target compounds (salting-out effect). In a separate set of experiments the effect of ionic strength on extraction was investigated. Experiments were carried out using 10 ml aqueous solutions spiked at 100 μg l^{-1} with MMT and having a salt content ranging from 0 to 30% (w/v) NaCl. Samples were extracted using each time a 2.5 μl octane drop exposed to the headspace for 5 min whilst applying a 1250 rpm agitation rate. Fig. 3 shows the results of this study. As can be seen, the response of the instrument increased when increasing the salt content of the aqueous samples. It appears that addition of NaCl in the aqueous solution enhanced extrac-

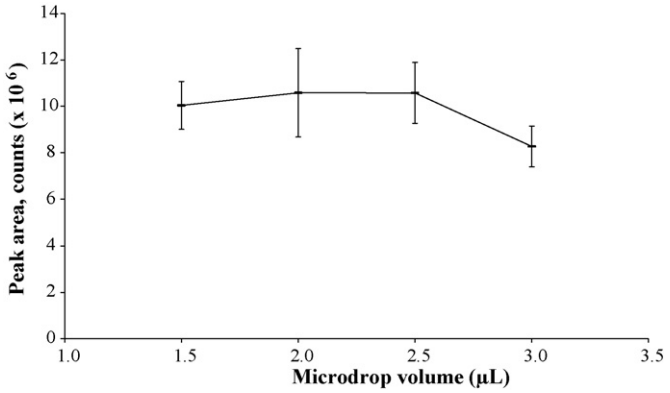

Fig. 1. Effect of drop volume on the extraction efficiency of headspace SDME used for the analysis of MMT in water samples. Other experimental conditions: 100 μg l^{-1} concentration level; 10 ml sample volume contained in 15 ml glass vial; 5 min sampling time; 1000 rpm stirring rate.

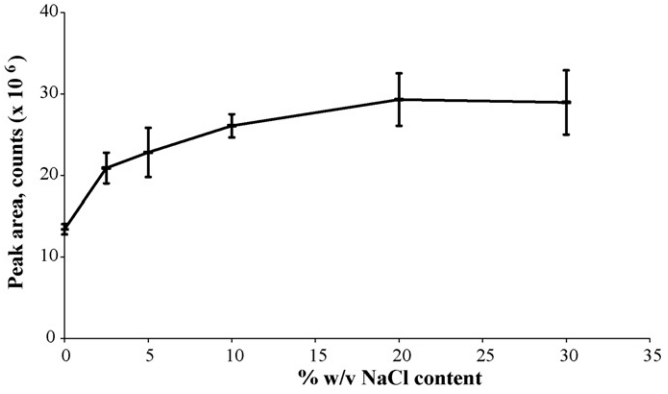

Fig. 3. Effect of ionic strength on the extraction efficiency of headspace SDME used for the analysis of MMT in water samples. Other experimental conditions: 100 μg l^{-1} concentration level; 10 ml sample volume in 15 ml glass vial; 2.5 μl octane drop; 5 min sampling time; 1250 rpm stirring rate.

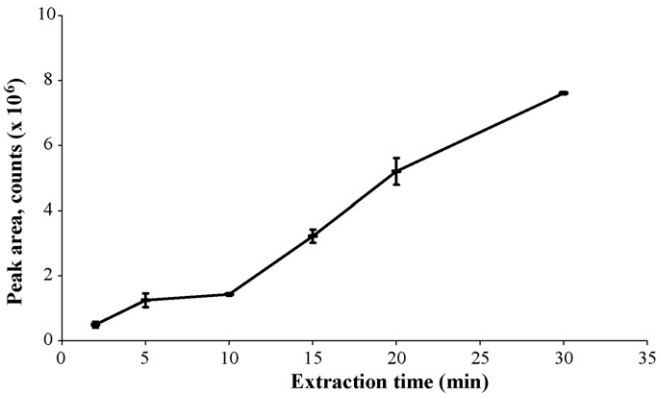

Fig. 4. Effect of sampling time on the extraction efficiency of headspace SDME used for the analysis of MMT in water samples. Other experimental conditions: 10 μg l^{-1} concentration level; 10 ml sample volume in 15 ml glass vial; 2.5 μl octane drop; 1250 rpm stirring rate; 20% (w/v) NaCl .

tion due to the salting-out effect where fewer water molecules are available for dissolving the analyte molecules, increasing thus the total amount of analytes transferred in the headspace and as such enhance extraction [24]. Accordingly a 20% (w/v) NaCl content was selected for all subsequent experiments.

Finally, the effect of sampling time upon extraction was investigated. During this set of experiments samples were spiked at 10 μg l^{-1} instead of 100 μg l^{-1} due to the high response of the instrument obtained with increased sampling times. Accordingly, each time a 2.5 μl octane drop was exposed to the headspace for a pre-set period of time (ranging between 2 and 30 min) of 10 ml aqueous sample containing 10 μg l^{-1} of MMT, having a 20% (w/v) NaCl content and stirred at 1250 rpm. Fig. 4 shows the response of the analytical instrument as a function of time. As can be seen, even after sampling the headspace of the spiked salted aqueous solutions for 30 min equilibrium is not attained. However, for the microdrop-based extraction methods equilibrium needs not to be attained [26]. It was decided to use a 20 min sampling time matching thus the chromatographic run and maximizing the sample throughput.

3.2. Performance of the headspace SDME method

The performance of the proposed method was evaluated using five concentration levels ranging from 0.1 to 25 μg l^{-1}. Samples were extracted under the optimized experimental conditions (2.5 μl octane drop exposed for 20 min to the headspace of a 10 ml aqueous solutions containing 20% (w/v) NaCl stirred at 1250 rpm). The calculated calibration curves gave a high level of linearity and the correlation coefficients (r) for MMT after conducting a 3-day study were found to be >0.9995. The limit of detection (LOD) for MMT was calculated by using the calibration curves and the Long and Winefordner criterion [27] and was calculated to be 0.21 μg l^{-1} (corresponding to approximately 53 ng l^{-1} when expressed as Mn). A previous report by Yang and Chau yielded a 0.3 pg l^{-1} (as Mn) detection limit for MMT in water samples whilst using SPME as a sample treatment method followed by gas chromatography-plasma atomic emission detection (a highly selective and sensitive detection tool for most elements) [9]. In addition, Fragueiro et al. recently published an analytical protocol based on SPME and direct thermal desorption–quartz furnace atomic absorption spectrometry and the authors reported a 0.71 μg l^{-1} (as Mn) detection limit of MMT in aqueous samples [10].

The repeatability of the proposed method expressed as relative standard deviation (R.S.D.), was evaluated by extracting five consecutive aqueous samples spiked at 1 μg l^{-1} under the optimized experimental conditions and was found to be 8.4%. Intra-day reproducibility was calculated by analyzing each day three aqueous solutions spiked at 1 μg l^{-1} with MMT for 3 consecutive days and the R.S.D. value found was 6.4%.

The enrichment factor defined as the ratio between the final analyte concentration in the organic acceptor phase and the initial aqueous sample concentration was found to be approximately 2100 after extracting for 20 min the headspace of a sample spiked at 1 μg l^{-1} with MMT. Furthermore, recovery, defined as the percentage of the amount of analyte extracted into the organic acceptor phase was found to be approximately 53%.

Finally, the effect of matrix on the proposed headspace SDME method was evaluated by extracting under the optimized experimental conditions five replicate samples of tap water and wastewater each one spiked at 1 μg l^{-1} with MMT. Relative recoveries (defined as the ratio of the concentrations found in environmental and deionized water samples spiked with the same amount of analyte) were 102% (R.S.D. = 17%) and 112% (R.S.D. = 12%) for tap water and wastewater, respectively. As expected using the headspace sampling mode resulted in a method that appeared not affected by the matrix of the aqueous samples.

4. Conclusions

A new analytical method comprising headspace SDME coupled with GC–MS has been developed, quantifying trace levels of MMT in water samples. Sample preparation time as well as consumption of toxic organic solvents was minimized without affecting the sensitivity of the method. This easy to use and cost-effective method represents an attractive alternative to traditional and recently introduced methods.

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