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Full automation of derivatization—solid-phase microextraction–gas chromatography–mass spectrometry with a dual-arm system for the determination of organometallic compounds in aqueous samples

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Abstract

The determination of organometallic compounds in aqueous samples by in-vial derivatization and headspace solid-phase microextraction (SPME)–gas chromatography (GC)–mass spectrometry (MS) has been fully automated using a Twin PAL dual-arm robotic system. Linearity, accuracy, sensitivity for a series of *n*-methyl, *n*-ethyl, and *n*-phenyl metal substituted chloride compounds of tin, lead, and mercury were investigated. The automated method was compared to similar manual methods and improved precision, speed and throughput was achieved. By originally programming the Twin PAL dual-arm system with the supplier's software (Cycle Composer, Version 1.5.0) the arms on the robot were only able to work in sequence. However, in order to have a flexible system and exploit time efficiently the robotic arms must work simultaneously. This was accomplished by programming the robot with the new software package called Cruise Control 4-2 for Twin PALs. Compared to Cycle Composer, Cruise Control 4-2 enhanced the speed and throughput of the automated system further. In addition, with a built-in crash prevention protocol and an improved user interface a more user-friendly system was obtained.

Keywords: Automation; Instrumentation; Solid-phase microextraction; Organometallic compounds

1. Introduction

The importance of determining organometallic compounds at trace levels in aqueous samples has been well documented in the literature [1]. Manual method extraction procedures and determination of organometallics in water by solid-phase microextraction (SPME) followed by gas chromatography (GC)–mass spectrometry (MS), GC flame ionization detection (FID) or GC inductively coupled plasma (ICP)-MS have been previously employed by others [2–7]. Both direct [8,9] and headspace [4] SPME methods have been contemplated and explored. Previous reviews [5] articulate that for metals such as tin, lead, and mercury, a derivatization process would increase the volatility of the resulting metal compounds such that headspace extraction would be possible. A variety of derivatizing agents have been employed to co-ordinate metal ions, thus, increasing the volatility of the species, promoting more to the sample headspace. Many methods have been used to derivatize organometallic compounds [10,11] including hydride generation and Grignard derivatization and lithiation schemes. However, the use of the tetraalkylborates has been seen as the most suitable when extractions from water samples are contemplated as this reagent can tolerate aqueous conditions [5]. Typical reactions that have been proposed for tin, lead, and mercury with sodium tetraethylborate are ascribed as:

$$3\mathrm{NaB(Et)_4} + \mathrm{RSn^{3+}} \rightarrow \mathrm{(Et)_3SnR} + 3\mathrm{Et_3B} + 3\mathrm{Na^+} \quad (1)$$

$$4\mathrm{NaB(Et)_4} + 2\mathrm{Pb^{2+}} \rightarrow \mathrm{Et_4Pb} + 4\mathrm{Et_3B} + \mathrm{Pb} + 4\mathrm{Na^+} \quad (2)$$

$$\mathrm{NaBEt_4} + \mathrm{RHg^+} \rightarrow \mathrm{EtHgR} + \mathrm{Et_3B} + \mathrm{Na^+} \quad (3)$$

where $\mathrm{Et} = \mathrm{C_2H_5}$. A number of metal species have been reported to be successfully derivatized by tetraethylborate and include: the mono-, di- and trichloride forms of methyl-, ethyl-, butyl-, phenyl-, and cyclohexyl- tin compounds [4,12]; poly-substituted methyl- and ethyl-lead compounds [3]; and methyl- and ethyl-mercury chlorides [2,13]. Other alkylborates have also been used. Sodium

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tetraphenylborate as a derivatization agent is now more preferred for aqueous mercury extractions [14] (utilized in the EPA guideline 600/4-91-0105) [15,16] over that of $K_3[Co(CN)_5CH_3]$ [17]. The majority of derivatizing agents (in particular, the sodium tetraethylborate salt) tend to be moisture and light sensitive, thus requires special handling [4]. Recent investigations [7] with different dry aprotic solvents, such as tetrahydrofuran (THF), have shown that the reagent stability can be improved if stored under cool (ca. 5 °C) conditions. It is, therefore, now possible to consider the use of extended automation techniques without the decomposition difficulties encountered when using such derivatizing agents. To incorporate such methods into an automation process in order to improve ease of preparation, to minimize laborious derivatization procedures, as well as to increase sample throughput, and to achieve greater reproducibility in the sample extraction and injection process, are desirable and enticing. Therefore, a Twin PAL system was investigated for automated derivatization and headspace SPME of some spiked and real organotin, organolead, and organomercury compounds from aqueous solutions followed by GC–MS. In addition, the flexibility, safety and user-friendliness of two different software packages (Cycle Composer and Cruise Control 4-2) were investigated.

2. Experimental

2.1. Chemicals and materials

THF (analytical grade) was obtained from Aldrich (Mississauga, ON, Canada) and was refluxed and dried over a sodium-benzophenone kettle in an anhydrous still according to standard procedure [18]. Water was obtained from Barnstead/Thermodyne NANO-pure ultrapure water system (Dubuque, IA, USA). Acetone (HPLC grade) and methanol (HPLC grade) were both acquired from Fisher Scientific (Springfield, NJ, USA). Triphenyltin chloride (95%), phenyltin trichloride (98%), trimethyltin chloride (98%), methyltin trichloride (98%), triethyltin chloride (98%), ethyltin trichloride (99%), lead(II) nitrate (99%), triethyllead chloride (99%), diphenyllead dichloride (98%), mercury(II) chloride (99%), dimethylmercury (99%), methylmercury(II) chloride (99%), diphenylmercury (96%), and phenylmercury chloride (96%) were purchased from Strem Chemicals (Newburyport, MA, USA), Aldrich or Alfa Aesar (Ward Hill, MA, USA) (depending upon availability). Sodium tetraethylborate ($NaBEt_4$, 80%) and sodium tetraphenylborate ($NaBPh_4$, 95%) were obtained from Strem Chemicals and stored at 5 °C in an airtight and N_2 purged containers until used. The SPME fiber used was a 100 μm poly(dimethylsiloxane) (PDMS) coated fiber obtained from Supelco (Bellefonte, PA, USA). Helium (99.999%) was obtained from Praxair (Waterloo, ON, Canada).

2.2. Description of automated system I and II

Two different automated methods (system I and II) were explored in this study. For both methods a Twin PAL dual-arm system, obtained from CTC (Zwingen, Switzerland), was used for automation. Fig. 1 shows a schematic drawing of the instrument, the location of the objects and the GC–MS. Fig. 1 shows that the two robotic arms had access to a needle heater, two sample heater/agitators, a sample tray, a cooled sample tray and a fast wash station. For system I, the upper arm (prep PAL) was designated to be the master and supported a magnetic vial transporting platform and a 20 μl syringe. The syringe had two side ports attached to two solution reservoirs; one containing water, and the other sodium acetate buffer solution. The syringe could be used to dispense up to 10 ml of solvent from the solvent reservoir. The lower arm (inject PAL) which controlled a magnetic vial transporting platform and a SPME fiber was designated as a slave to the upper arm. System I was connected to a Star CP-3800 GC-ion trap Saturn 2000 MS system from Varian (Mississauga, Canada) and programmed using Cycle Composer Version 1.5.0 (obtained from CTC Analytics). System II was connected to a 5973 Network MSD from Agilent Technologies (Mississauga, Canada) and programmed using Cruise Control 4-2 from Leap Technologies (Carborro, NC, USA). In addition, the 20 μl syringe used in system I was replaced with a standard 1 ml glass syringe. Furthermore, the mass spectrometric and chromatographic parameters used in this work are enlisted in Table 1.

2.3. Solutions

Standard samples were prepared in 10 ml vials either manually or with the use of the automated PAL system. Both Cycle Composer and Cruise Control 4-2 allowed the sample preparation arm of the Twin PAL system to prepare diluted samples from a stock metal solution. All solutions of the derivatization agent, 20% (w/w), were prepared by a method outlined by Schubert et al. [7]. A number of real aqueous samples with known concentrations of tin, lead and mercury were acquired from an Ecosystem Proficiency testing QA program for trace elements in surface waters, Study FP80-Spring 2002 (carried out at the National Water Research Institute (Burlington, ON, Canada)). These samples are further described elsewhere [19].

2.4. Safety issues

The organometallic compounds used in this study are highly toxic. Thus, they were handled carefully inside a N_2 filled glove bag positioned in a fume hood. All solutions and standards were stored in metal containers at 2 °C when not in use. $NaBEt_4$ is hygroscopic, air/moisture sensitive and flammable; therefore, it was handled only in a glove bag under inert gas atmosphere. As it may cause irritations or burns

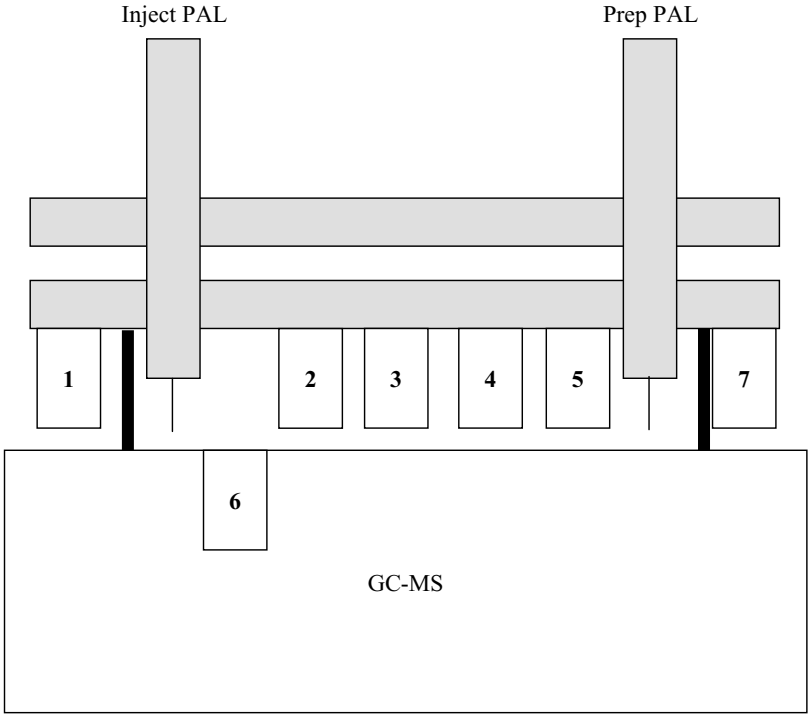

Fig. 1. Drawing of the Twin PAL dual arm system. 1, sample heater/agitator; 2, fiber heater; 3, cooled sample tray; 4, sample tray; 5, fast wash station; 6, GC injector port; and 7, sample heater/agitator 2.

Table 1
Optimized GC–MS parameters for the automated and manual derivatized tin, lead, and mercury analysis

Parameters	Tin	Lead	Mercury
GC			
Desorption (min)	1	1	
Injector (°C)	250	250	250
Run time (min)	13	13	12
Column	Hold at 40 °C for 1 min, to 220 °C at 20 °C/min, hold for 3 min at 220 °C	Hold at 40 °C for 1 min, to 220 °C at 20 °C/min, hold for 3 min at 220 °C	Hold at 40 °C for 1 min, to 80 °C at 10 °C/min, hold for 2 min at 80 °C, to 125 °C at 15 °C/min, hold for 2 min at 125 °C
MS			
Transfer line (°C)	260	260	260
Manifold (°C)	50	50	50
Trap (°C)	150	150	150
Scan range (*m/z*)	40–450	40–450	40–450

on contact with skin or eyes, gloves, lab coat, and safety goggles were worn when working with this compound.

3. Results and discussion

3.1. Critical considerations

Under extended automation conditions the stability of the derivatization agent is imperative. Alkylborates undergo hydrolysis readily and are slightly heat sensitive. In water, the reagent is very unstable, so fresh reagent had to be prepared daily [4]. By dissolving the reagent in dry THF, prolonged stability of the derivatizing agent was achieved. Stored at 27 and at 5 °C the reagent (20% solution) was stable for 2 and 4 weeks, respectively. Investigations showed that the THF peak, the residuals left from the derivatization reaction (sodium alkylborate or THF-derivative complexes) did not overlap with any of the metallic derivatized species in the chromatogram (results not shown). The 100 μm PDMS fiber appeared to be inert to both THF and to the alkylborate derivative complexes. Seventy five extractions were performed using the same fiber without noticeable background degradation products in the chromatogram or

visible damage to the SPME fiber. However, column contamination is possible with such reactions, thus the GC–MS must be baked out periodically to remove such residual backgrounds. The alkylation reactions of organometallic compounds using alkylborates are pH dependent with an optimum pH between 4 and 5 [4,7]. In our analysis, a pH range of 4.0–4.3 was maintained by introducing a sodium acetate/acetic acid buffer (1 ml) to each sample prior to addition of the derivatizing agent.

3.2. Development of automation: system I

The Twin PAL dual-arm system I was programmed and controlled by running two Cycle Composers. The Cycle Composer running the PAL equipped with the SPME fiber (inject PAL) controlled the parameter settings for the sample heater/agitator (reaction/extraction), the thermal desorption and the fiber bake out. The other Cycle Composer running the PAL equipped with the syringe (prep PAL) controlled all parameter settings for the addition of buffer and reagent to the sample vial and the movement of the sample vial to the sample heater/mixer 2. In order to prevent crashes between the arms, a certain vial position in the sample tray (32) was designated as common and accessible to both arms. However, as the software did not allow the two arms to work in a simultaneous fashion, but only sequentially, collisions between the arms were not a major problem.

The syringe was cleaned between each use by movement of the arm to a fast wash station. After cleaning the syringe, the prep PAL first added 1 ml of buffer to the sample vial, and then moved the sample vial to the heater/agitator so that it could be mixed for a required time period. The sample vial was then brought back to the original sample queue position. The prep PAL moved to the vial holding the stock derivatization agent (maintained at 5 °C), and its syringe aspirated the required volume from this vial, and then positioned itself to dispense the derivatization volume (1 ml) into the previously prepared buffered sample vial. The total volume in the vial was now 6 ml, which was ideal for headspace extraction from a 10 ml vial. This vial was transported to position 32, whereupon the inject PAL transferred the sample from position 32 to the heater/agitator module. The solution was agitated for an optimized time at a particular speed to allow the derivatization. After the reaction, the temperature was raised and the agitation adjusted to the optimized presets for the extraction. The inject PAL moved so that the syringe could puncture the vial septum and expose the fiber to the optimized sampling depth, and begin a heated/agitated headspace extraction for the required time. When the extraction time was completed, the inject PAL detracted the exposed fiber and the arm moved to the GC injection port to inject and expose the SPME fiber for the required desorption time. The GC injection also triggered the computer program on the GC–MS instrument to start the accumulation of data for the analysis. When the desorption time had elapsed, the inject PAL detracted the fiber and moved away from the GC injection port. The arm then transferred the sampled vial from the heater/agitator module to position 32 in the sample queue rack. Finally, the inject PAL moved to the needle heater for fiber bake out for a required amount of time at a designated temperature. By using this method, any analyte which might carry over to the next run was removed. While the inject PAL was positioned at the needle heater, the prep PAL picked up the vial from position 32 and placed it back into the original vial position in the queue. The prep PAL then moved to the next vial in the sample queue to be analyzed and the above cycle was repeated. The method sequence was also synchronized so that the GC–MS instrument analysis runtime and stabilization would be finished before injection of the next sample in the queue.

3.3. Optimization

As part of system optimization a number of variables were examined, including reaction time, equilibration time and sample carry over. The impact of different reaction times (1, 2, 5, 10, 15, 20, 25, 30, 40, 60, 90, and 120 min) on amount extracted was investigated for the following organometallic species (triphenyltin chloride, phenyltin trichloride, trimethyltin chloride, methyltin trichloride, triethyltin chloride, and ethyltin trichloride, lead(II) nitrate, triethyllead chloride, diphenyllead chloride, mercury(II) chloride, methylmercury(II) chloride, dimethylmercury, phenylmercury chloride and diphenylmercury). The results are listed in Table 2 (based on the slowest derivatization reaction in each group of metals). Furthermore, the time needed to reach equilibrium ($t_{95\%}$) was also investigated. The extraction time profile for some tin species (Fig. 2) and a lead species (Fig. 3) were determined. It was found that the lead species and the tin species reached equilibrium around 10 and 5 min, respectively. Organo-mercury compounds equilibrated even faster (results not shown), as these compounds are more volatile than organo-lead and -tin. The time it takes to reach equilibrium is controlled by the thickness of the boundary layer [20], which again

Table 2
Optimized parameters used for dual-arm Twin PAL automation method program for tin, lead, and mercury analysis

	Tin	Lead	Mercury
Derivatization with diluter 20 μl syringe			
Syringe wash cycles	3	3	3
Volume of buffer added (ml)	1	1	1
Agitation speed (rpm)	750	750	750
Temperature (°C)	40	40	40
Mixing time for buffer (min)	3	3	3
Syringe wash cycles	3	3	3
Derivatization agent added (%)	5	5	5
Derivatization agent added (μl)	20	20	20
Agitation speed (rpm)	750	750	750
Temperature (°C)	60	60	60
Reaction time (min)	9	20	10

100 μm PDMS fiber; 10 ml vial.

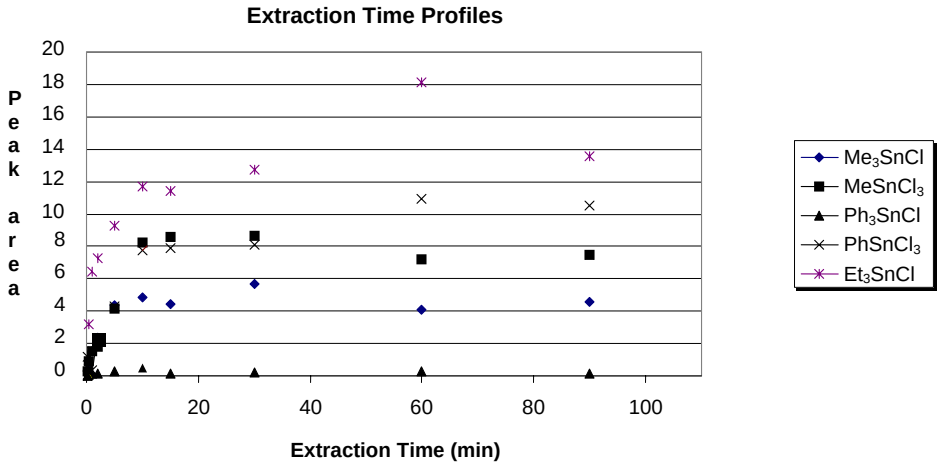

Fig. 2. Headspace extraction time profiles of various tin species (20 μg/l) using 100 μm PDMS fiber.

is controlled by the agitation of the sample. In order to ensure that the agitation obtained with the heater/agitator module was as efficient as stirring with a stir bar, the extraction time profile for naphthalene was determined using both agitation techniques. Results showed that the equilibration time profiles were more or less indistinguishable (results not shown), indicating that the level of agitation obtained was the same. The extraction times used in this study for the different metals are listed in Table 3. It has been reported that carryover or memory effect is a problem encountered in the analysis of metals, like mercury, using both conventional techniques [10,13] and with SPME methods [21,22]. Carryover was not considered a problem as long as the fiber was baked out at 250 °C for 3 min resulting in less than 1% carryover. However, the fiber was left in the needle heater for 15 min, awaiting the next sample to be prepared by the prep PAL, ensuing the minimization of carryover.

Table 3
Optimized parameters used for the SPME in the automation method program for tin, lead, and mercury analysis

	Tin	Lead	Mercury
Total volume in vial (ml)	6	6	6
Vial penetration depth (mm)	24	24	24
Extraction time (min)	5	10	3
Extraction temperature (°C)	60	60	60
Extraction agitation speed (rpm)	750	750	750
Desorption time (min)	1	1	1
Bakeout time (min)	15	15	15
Bakeout temperature (°C)	250	250	250

100 μm PDMS fiber, 10 ml vial.

3.4. Evaluation

The linear range and the detection limit were determined for both mixed metal samples and single metal samples.

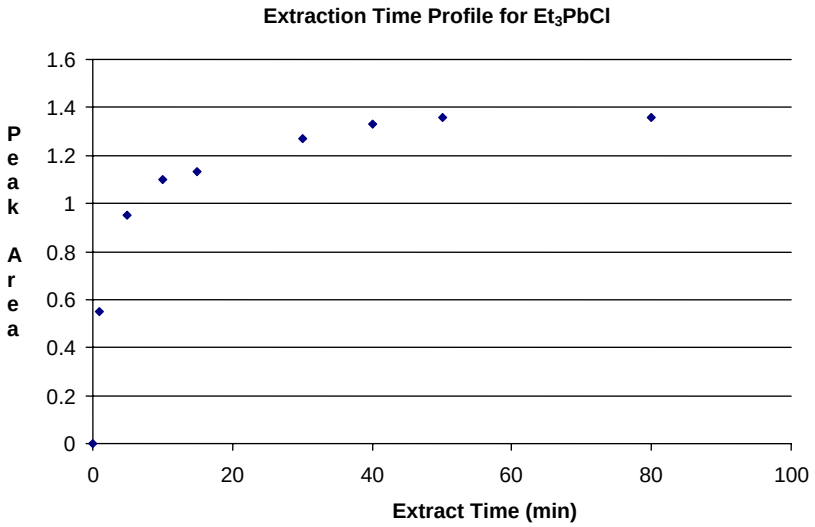

Fig. 3. Headspace extraction time profile of Et_3PbCl (20 μg/l) using 100 μm PDMS fiber.

Table 4
Linear ranges and detection limits for spiked samples for automated tin, lead, and mercury analysis in a mixed metal solutions and as single metal solutions

	Tin, mixed[a]/single[b]	Lead, mixed[a]/single[b]	Mercury, mixed[a]/single[b]
Linear range (mg/l)	20–650/15–600	18–80,000/15–80,000	25–2500/22–3000
Correlation coefficient (r)	0.996	0.994	0.999
Reference[c]	N.A./20–420 [7]	N.A./20–100,000 [3]	N.A./25–2500 [14]
Detection Limit (μg/l)	1.3/0.9	1.4/0.7	1.3/0.3
Reference[c]	N.A./0.02 [7]	N.A./0.20 [3]	N.A./0.075 [14]

[a] Mixed metal detection limits were determined by the poorest detected metal, in most cases they were the multi-substituted phenyl metal compounds.
[b] Single metals used were: Et_3Sn^+; Et_3Pb^+; $MeHg^+$ by ion trap MS. Note Cai and Bayona [14] used tetraethyl lead for the mercury compound.
[c] References use FID [3,7] or SIM-MS [14].

The results obtained are shown in Table 4 together with the results obtained by others. The results in Table 4 show that the linearity and the sensitivity of the automated derivatization SPME–GC–MS methods were comparable to what has previously been found for manual derivatization SPME–GC–MS methods. The detection limit was calculated using the formula $Y_{DL} = Y_B + 3S_B$) [23] were Y_{DL}, Y_B, and S_B are the signals of the detection limit, blank signal, and standard deviation of the blank, respectively. At the time of the study, no certified water samples containing tin, lead or mercury were available. However, a number of metal samples were obtained from National Water Research Institute in Canada as part of the ICP round robin study [19]. In this study, several analytical laboratories assessed the metal concentration in a number of environmental samples and the means and their associated standard deviations (3S.D.) obtained for the individual metal analysis are reported in Table 5. The number of laboratories involved was $N = 15$ for tin, $N = 29$ for lead and $N = 15$ for mercury. Our data, included in the same Table, were the results of three sample replicates for each metal analysis, and were achieved using similar conditions as outlined in Tables 1–3. The data obtained from the automated derivatization—SPME–GC–MS technique gave results (for those samples which were above our analyses detection limits) which were similar to those obtained by standard ICP analysis, clearly showing that the accuracy of the method was good (Table 5).

Table 5
Comparison of ICP to automated derivatization—SPME–GC–MS results for the analysis of tin, lead, and mercury in some environmental samples

Samples	Tin		Lead		Mercury	
	Det[a]	Found[b]	Det[a]	Found[b]	Det[a]	Found[b]
Spiked and diluted tap water I	2.7	2.6	3.3	3.4	–	–
3S.D.	0.83	0.09	0.87	0.25		
Long lake, Sudbury	1.5	1.3	11.6	11.2	–	–
3S.D.	0.30	0.8	2.80	0.43		
Rainwater, Grimsby	0.8	1.0	0.28	<0.7	–	–
3S.D.	0.28	0.56	0.072	–		
Spiked and diluted tap water II	23.4	23.8	34.5	34.1	–	–
3S.D.	6.49	4.21	4.77	2.34	–	–
Mercury in water	–	–	–	–	0.39	0.31
3S.D.	–	–	–	–	0.09	0.21

<: not detected, detection limit reported.
[a] Det: determined by ICP analysis, reported in μg/l, where $n = 15$ for tin, $n = 29$ for lead, and $n = 15$ for mercury (taken from [19]).
[b] Found: determined by derivatization with $NaB(Ph)_4$-SPME–GC–MS analysis, reported in μg/l, were $n = 3$ for all analysis.

3.5. Development of automation: system II

System II was programmed using Cruise Control 4-2, a software package that was developed in order to control both PALs simultaneously with only one program. The optimized parameter settings established in system I was also used in system II (see Table 1 for details) unless otherwise stated. The syringe (now with a volume of 1 ml) was cleaned at the start of each cycle and after each use using pure water at the fast wash station. First, the prep PAL moved over to the vial containing the buffer, aspirating 1 ml into the syringe before moving over to the sample vial and dispensing the solution. The buffered sample was not mixed at this point and the sample heater/agitator 2 was removed from the instrument setup which was different from system I (Fig. 1). Instead, the prep PAL moved over to the cooled sample tray (2 °C), aspirating the reagent into the syringe before moving over to the sample vial and dispensing the solution. Following this, the inject PAL picked up the vial and transferred it to the sample heater/agitator for the designated time and temperature. The SPME fiber was then exposed to the headspace of the sample and extraction was performed for a required amount of time. Cruise Control 4-2 then called up a Chem Station method and prepared the system for injection. The inject PAL then moved over to the GC injector for thermal desorption before transferring the sample vial back to the tray. Finally, the inject PAL moved over to the needle heater for fiber bake out (250 °C) for 3 min, as opposed to 15 min used in system I.

3.6. Benefits of Cruise Control 4-2

Cruise Control 4-2 allowed both PALs to work together leading to an enhanced risk of collision between the arms. Therefore, Cruise Control 4-2 was developed with an integrated security protocol that made collisions impossible.

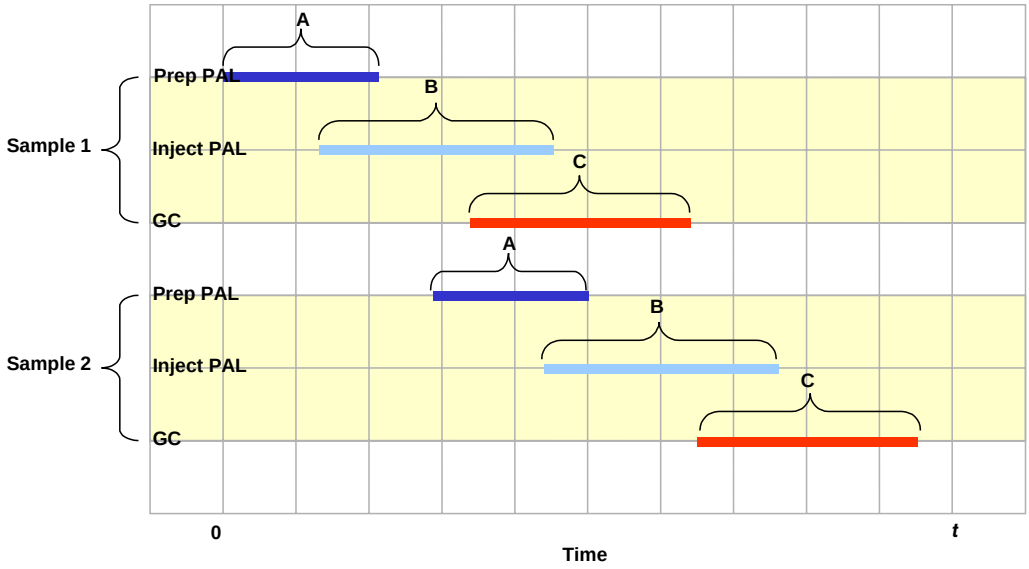

Fig. 4. Time chart of the automated system programmed with Cruise Control 4-2. A = 6 min and 10 s, B = 18 min and 45 s, and C = 18 min and 40 s.

A collision between the arms is not necessarily fatal to the hardware, but a collision will push the arms out of position and when the arms are out of position, the various objects will not be located. If the syringe or the SPME arm misses its target, the result is usually a broken needle/fiber. As mentioned above, the major benefit of the Cruise Control 4-2 was that both arms could be programmed to work simultaneously. Fig. 4 illustrates how the PALs and the GC work simultaneously in this automated method, clearly using time more efficiently than if working sequentially as with system I. The time segments A, B, and C (Fig. 4) represent 6 min and 10 s, 18 min and 45 s, and 18 min and 40 s, respectively, for the analysis of methylmercurychloride. If the segments A and B were performed consecutively as in system I with the use of Cycle Composer, a total sample preparation time of 24 min and 55 s had been required. By using both robotic arms simultaneously (system II) a sample preparation time of only 18 min and 45 s was required, a reduction of 6 min and 10 s or 24% of the total analysis time. In this way, efficiency was increased so that speed and throughput could be enhanced even further. The GC analysis time was 18 min and 40 s (run time + cooling time, segment C in Fig. 4) which was almost identical to the time needed by the inject PAL to have the next sample ready. Therefore, both the GC and the inject PAL were running constantly (see Fig. 4). The coordination of the GC and inject PAL could only be maintained if the prep PAL started 90 s before the GC was ready, having the next sample completed just before inject PAL was finished baking out after the previous analysis (see Fig. 4). If the prep PAL made the solution ready for reaction/extraction too early, the R.S.D. increased. By reducing the time lag between addition of the reagent and mixing of the sample from 300 to 10 s the R.S.D. value was improved from 7 to 1.4% (tested for methylmercurychloride). Finally, the precision was investigated for this system, the automated system programmed with Cycle Composer and a manual SPME method. The R.S.D. ($N = 3$) for the analysis of organo-mercury, -tin and -lead are shown in Table 6. Clearly, automation results in improved precision (R.S.D. in the range 1.2–3.5%) compared to manual methods (R.S.D. in the range 5.3–8.2%). No significant difference between the two automated systems was found regarding precision.

Table 6
Comparison of R.S.D. ($n = 3$) values obtained for the manual SPME method and the two automated SPME methods (systems I and II)

Method	Hg (R.S.D., %)	Sn (R.S.D., %)	Pb (R.S.D., %)
Manual[a]	8.2	5.3	7.5
Automated (system I)	2.0	1.2	2.6
Automated (system II)[a]	1.4	1.7	3.2

[a] Total volume in-vial 2.5 ml.

4. Conclusions

This study demonstrates that Twin PAL dual-arm system can be used to automate the determination of organometallic compounds by in-vial derivatization headspace SPME–GC–MS. Linearity, accuracy and detection limits obtained using an automated systems were comparable to those achieved by manual derivatized—SPME–GC–MS and GC–FID techniques. The precision was improved for the automated method compared to the manual method for all organometallic compounds investigated. Automation was investigated through programming the robotic system with either Cycle Composer or Cruise Control 4-2 software packages. Cruise Control 4-2 was superior in that it prevented crashes between the arms, allowed higher throughput and simplified the user interface.

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