Speciation without chromatography

Part 2. †Determination of tributyltin by chloride generation flow injection atomic absorption spectrometry‡

Christine Scriver,* Zoltán Mester, Ralph E. Sturgeon, László Péter§ and Scott Willie

Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9. E-mail: Christine.scriver@nrc.ca

A procedure is described for the quantitation of tributyltin in aqueous samples and extracts based on its relatively high volatility in halide media, permitting vapour phase sampling from the headspace above such samples. Tributyltin chloride (TBT-Cl) was purged from various chloride containing aqueous matrices and collected on the surface of an iridium treated graphite tube for subsequent quantitation by graphite furnace atomic absorption. Iodide, bromide and chloride matrices were compared for their generation efficiency. The effect of acidity of the sample was also studied. An absolute detection limit of 1.3 ng TBT (as tin) was estimated, corresponding to a detection limit of 0.33 ng ml^{-1} for a 4 ml sub-sample. Method validation was achieved using NRCC PACS-2 (sediment) Certified Reference Material, for which reasonable agreement between certified and measured values of tributyltin content was obtained. A procedural concentration limit of detection of 66 ng g^{-1} TBT in the sediment could be achieved.

Introduction

The determination of organometallic pollutants is critical to environmental health studies. Over the last twenty years, various analytical strategies have been developed for trace element speciation, employing almost exclusively chromatographic separation in tandem with element/molecular specific detectors. The only elemental exception is mercury, where considerable effort has been made to develop 'chromatography free' sequential extraction/trapping schemes for differentiation of elemental, inorganic and organomercury species.[1,2] Modern tandem analytical systems for speciation represent the state-of-the-art of measurement science; however, most of them are unsuitable for quality control purposes in commercial settings because of their complexity, low sample throughput, *etc.* To address these concerns, European scientists have recently developed a compact measurement system designed specifically for speciation analysis.[3] In Part 1 of this article,[4] and an earlier communication from this laboratory,[5] it was shown that volatile/semi-volatile (organo)metal halide species can be generated in both laboratory and natural settings. In the headspace above a halide rich aqueous medium, semi-volatile organometallic halide species are clearly present. This has been demonstrated by determination of TBT[5] and methylmercury[6] in aqueous solutions by sampling the headspace above the liquid using solid-phase microextraction (SPME). The collected TBT and methylmercury halide species were determined by inductively coupled plasma time-of-flight mass spectrometry.

SPME is a passive sampling, equilibrium-based, extraction approach, and the amount of analyte extracted from the sample is thus relatively small. More sensitive measurements should be possible with use of an exhaustive extraction approach where all of the analyte present in the sample solution is trapped in/on a suitable extraction medium. To increase the rate of release of TBT-Cl from the solution into the headspace, continuous purging can be employed through a gas–liquid separator (GLS). Using this approach, the TBT-Cl species was sequestered within a graphite furnace, in a manner similar to that in earlier work by Sturgeon *et al.*,[7] wherein tin hydride was sequestered in an iridium pre-treated graphite tube.

This study describes the development of a technique based on *in-situ* trapping of TBT as volatile TBT-Cl using flow injection coupled to graphite furnace atomic absorption spectrometry (FI-GFAAS). Method parameters are optimized and figures of merit presented. The methodology was validated through quantitation of TBT in NRC Certified Reference Material marine sediment PACS-2.

Experimental

Instrumentation

Analytical measurements were performed using a PerkinElmer Model 4100Z transversely heated graphite furnace atomic absorption (THGA) spectrometer fitted with an AS-70 auto-sampler. The spectrometer was interfaced to a Model 400 flow injection system (FIAS) and an AS-90 autosampler, as schematically illustrated in Fig. 1. A Teflon (1 mm id) sample transfer line was heated to 65 °C using heater tape powered by a Variac. The transfer line terminated in a quartz tip, which could be inserted through the sample introduction hole in the graphite tube to allow the TBT-Cl to be deposited on an Ir-coated surface, which was preheated to 300 °C. A Sn hollow cathode lamp (SCP Science, Montreal) operating at 14 mA served as the radiation source.

The sample was pumped directly to the gas–liquid separator (GLS) at a rate of 2 ml min^{-1}, where it was merged with an Ar purge gas. The Ar gas flow rate, 200 ml min^{-1}, was used to aid liberation of the TBT-Cl species from the sample solution.

A Microdigest Model 401 (2.45 GHz, maximum power 300 W) microwave digester (Prolabo, Paris, France) equipped with a TX32 programmer was used for microwave-assisted extraction of butyltins from the sediment.

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§Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1525 Budapest, P.O.Box 49, Hungary.
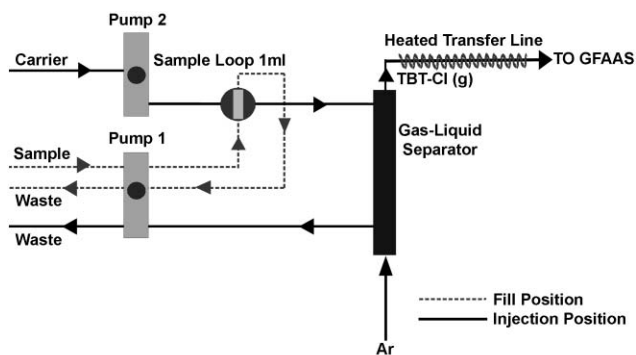
Fig. 1 Schematic of the FI–THGA system.

Reagents

Tributyltin chloride (TBT), dibutyltin chloride (DBT) and monobutyltin chloride (MBT) were obtained from Alfa Aesar (Ward Hill, MA, USA). Stock solutions (1000 mg l^{-1}) were prepared by dissolution of the pure compounds in sub-boiling distilled methanol obtained from EM Science (Merck, Germany). An inorganic tin standard was prepared by dissolving high purity tin shot in 2 M HCl. The THGA tube was coated each day (or more frequently if any liquid from the GLS inadvertently entered the transfer line and was transported to the THGA) with a permanent Ir modifier (25 μl aliquot of a 10000 ppm Ir solution, Alfa Aesar) following the procedure of Sinemus et al.[9] Solutions of NaCl (EM Science) of varying molarity were prepared. Test solutions of MBT, DBT and inorganic Sn were prepared by dilution of the stock solutions with 2 M HCl. De-ionized water (DW) from a Nanopure system (Barnstead/Thermolyne, Boston, MA, USA) was used for the preparation all solutions. Acetic, hydrochloric and nitric acids were purified in-house by sub-boiling distillation of reagent grade feedstocks using a quartz still.

All organotin stock and sample solutions were stored in Pyrex volumetric flasks under refrigeration until analyzed. Acid and NaCl solutions were stored in polypropylene bottles at room temperature. The marine sediment Certified Reference Material (CRM) PACS-2, from the National Research Council of Canada,[10] was used for validation of the technique.

Procedure

Samples were processed using a 1.0 ml fixed loop volume injection. Table 1 (a) summarizes the programmed steps for the FIAS module. Sample fills the sample loop and line during the prefill and step 1. During step 2, the FIAS-furnace program switches the FIAS valve and moves the autosampler arm into the furnace for subsequent analyte deposition. Tributyltin

chloride is generated during steps 3 and 4, propelled by 2 M HCl carrier, and transported to the furnace in a flow of Ar. The 1.0 ml sample loop and generation time may vary, depending on the sample, dilution and detection limit desired. The autosampler arm is returned to its original position and the valve is switched back to the fill position in step 5. Step 6 flushes the GLS with carrier. The furnace program, summarized in Table 1 (b), heats the sequestered sample for 10 s at 300 °C while purging the tube with Ar at a flow rate of 250 ml min^{-1}, before rapid heating to the atomization temperature of 2200 °C for 3 s. A final clean-out step of 2300 °C for 2 s completes the procedure.

The performance of the method was evaluated by analysis of PACS-2 sediment Certified Reference Material. A microwave assisted leaching procedure was applied for extraction of TBT from the sediment, as described elsewhere.[8] In short, 2 g of the sediment were placed into the extraction vessel and 40 ml of concentrated acetic acid were used as the leaching medium. The acidified sample was heated in a Prolabo microwave digester at 60% power for 3 min. The contents were centrifuged at 2000 rpm for 5 min and the supernatant was transferred to a vial. A 5 ml aliquot of this solution was diluted with 20 ml of 2 M HCl to ensure a low pH and sufficient concentration of chloride. This solution was used for analysis.

Results and discussion

At sufficiently low concentrations, TBT is present in ionic form in solution and in order to ensure efficient volatilization, the corresponding chloride species must be formed.[5] Introduction of Cl^- into the system promotes the formation of neutral TBT-Cl species, which has a relatively high vapour pressure. In this study, the effects of solution composition, purging, and trapping parameters on analytical response were investigated. Experiments were also performed to evaluate the selectivity of the procedure, in order to discern how efficiently the method is able to discriminate TBT from other butyltin and inorganic tin species that may be present in the sample.

Trapping of TBT-Cl

The optimum trapping temperature and nature of the graphite tube were determined first; the effect of trapping temperature when using both iridium coated and uncoated graphite tubes. With an untreated graphite tube, virtually no adsorption/trapping occurs, which may arise as a consequence of the relatively low surface area of the pyrolytic graphite coated medium. The iridium treated tube exhibits superior sequestration capability at higher temperatures, likely due to the catalytic decomposition of TBT-Cl on the graphite surface promoted by the presence of iridium. The effect of various

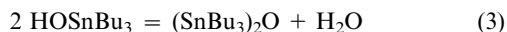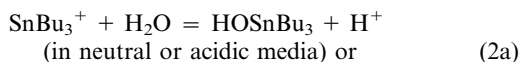**Table 1** FIAS[a] and THGA programs for sample introduction/collection and atomization

(a) Step	Time/s	Pump 1/rpm	Pump 2/rpm	Valve
Prefill	5	60	60	Fill
1	20	60	60	Fill
2	8	0	0	Inject
3	30	60	60	Inject
4	20	60	60	Inject
5	8	0	0	Inject
6	3	40	40	Fill

(b) Step	Temperature/°C	Ramp/s	Hold/s	Gas flow
1	300	1	10	250
2	2200	0	3	0
3	2300	1	2	250

[a] Injection Temperature 300 °C.

platinum metal modifiers on the trapping efficiency of volatile metals on treated graphite surfaces has been discussed elsewhere.[7] There was little change in response in the range 300–400 °C. A deposition temperature of 300 °C was used for further experimentation. Fig. 2 presents typical transient signals arising from 25 ng of TBT-Cl trapped at 300 °C on an untreated graphite tube and on an iridium treated graphite tube. The well-defined narrow signal arising from the uncoated tube may result from the rapid vaporization of molecular TBT-Cl from its surface. This is consistent with the low trapping efficiency, wherein the species likely remain intact following simple adsorption and release from the graphite surface with atomization subsequently occurring in the gas phase. This is in sharp contrast to the release characteristics from the iridium treated tube, where the resulting transient signal is much broader and less well defined. In this system, trapping of the TBT may arise as a result of catalytic reduction of volatile TBT-Cl to a less volatile inorganic complex bound to the iridium surface. Release of analyte from the coated tube occurs at a higher temperature (later time) and the broader signal reflects a strong interaction of the tin with the reduced iridium, either through a physical diffusion process or a consequence of strong chemical interaction.

Formation of TBT chloride in aqueous solutions

The following equilibria should be taken into account for TBT "dissolved" in aqueous media:

$$ClSnBu_3 = Cl^- + SnBu_3^+ \qquad (1)$$

$$SnBu_3^+ + H_2O = HOSnBu_3 + H^+$$
$$\text{(in neutral or acidic media) or} \qquad (2a)$$

$$SnBu_3^+ + OH^- = HOSnBu_3 \text{ (in alkaline media)} \quad (2b)$$

$$2\,HOSnBu_3 = (SnBu_3)_2O + H_2O \qquad (3)$$

The dimerization illustrated in reaction 3 can be neglected since it is expected to be very unstable as a result of large steric hindrance arising from the six butyl chains. Furthermore, the non-polar dimer can only be weakly solvated as compared to the species containing a hydroxyl group.

If the TBT in solution is in equilibrium with that in the headspace gas phase, electrically neutral species such as $ClSnBu_3$ and $HOSnBu_3$ will be present in the gas phase as well. It is anticipated that the vapour pressure of $HOSnBu_3$ is much lower than that of $ClSnBu_3$ because the hydrogen bonds formed by the –OH group may impart extra stability to the solution phase species. For this same reason, it is assumed that the equilibrium vapour pressure of the hydrated $HOSnBu_3$ is significantly lower than that of $ClSnBu_3$.

The concentration of Sn-containing species in the gas phase

must be considered as a sum of the Sn concentration originating from both species. Considering the dissociation of TBT in the liquid phase, from eqn. 1 we have:

$$K_1 = [SnBu_3^+][Cl^-]/[ClSnBu_3] = [Cl^-]\alpha/(1-\alpha) \qquad (4)$$

where α is the degree of dissociation (*i.e.*, = [TB]/([TB] + [TBT])). As it is TBT in the gas phase that is the measurand, its concentration (or partial pressure) is related to the TBT solution concentration *via* Henry's law, *i.e.*:

$$(ClSnBu_3)_G = p_1(1-\alpha) = p_1[Cl^-]/(K_1 + [Cl^-]) \qquad (5)$$

where the subscript refers to a species in the gas phase and p_1 is constant. It can be seen that the term on the right-hand side of eqn. 5 approaches p_1 if the chloride concentration is made sufficiently high.

A similar line of thought yields the gas-phase concentration of $HOSnBu_3$. The concentration of the hydroxyl species is proportional to the amount of dissolved TBT and the degree of hydrolysis. The vapour pressure of the hydroxyl form is thus expressed as:

$$(HOSnBu_3)_G = p_2 K_2/(K_2 + [Cl^-]) \qquad (6)$$

Hence, the overall "Sn" concentration in the gas phase can be approximated by eqn. 5, as the detector response differs from $(Sn)_G$ by a constant factor only.

Assuming that the $SnBu_3$–Cl association reaction is not a rate limiting step, and in the absence of knowledge concerning the rate at which the headspace is equilibrated, *i.e.*, the kinetics characterizing the phase transition process, the concentration of this species in the gas phase above the solution is given by:

$$(ClSnBu_3)_G = k_1[Cl^-]/(K_1 + [Cl^-]) \qquad (7)$$

where k_1 is the rate constant characterizing the mass transfer of analyte to the gas phase.

Whether the analysis is achieved under equilibrium or kinetic regimes for the phase transfer process can be discerned by the effect of the Ar carrier gas flow rate on the response.

The analysis also shows that for any given TBT concentration studied, a 2 M solution of NaCl cannot completely suppress the dissociation and/or hydrolysis of TBT, with the consequence that the maximum theoretical efficiency with which the analyte can be transferred from the gas phase is 87%. The experimentally obtained effieciency, derived from a comparison of the integrated absorbance obtained from the tin concentration in the feed solution as opposed to the waste solution, was 40 ± 10%. The somewhat lower measured efficiency is likely a consquence of the limited efficiency with which the volatile TBT-Cl is transferred from the liquid to the gas phase in this flow system.

Eqn. 7 is based on the assumption that the gas–liquid partitioning is a first-order process with respect to the concentration of the species in the liquid phase. It can be seen that, in both cases, the resulting signal intensity (*I*) can be evaluated by the same function, although the constants may have different meaning:

$$I = A + B[Cl^-]/(K_1 + [Cl^-]) \qquad (8)$$

Fig. 3 presents the response as a function of chloride concentration in the solution. The broken line is calculated using eqn. 8. The parameters A and B comprise several factors (vapour pressure of the two species and/or kinetic constants, as well as atomic absorption coefficients), and hence their values provide no information concerning equilibrium in the liquid phase. However, K_1 can be correctly determined, regardless of the nature of the processes preceding the collection of the
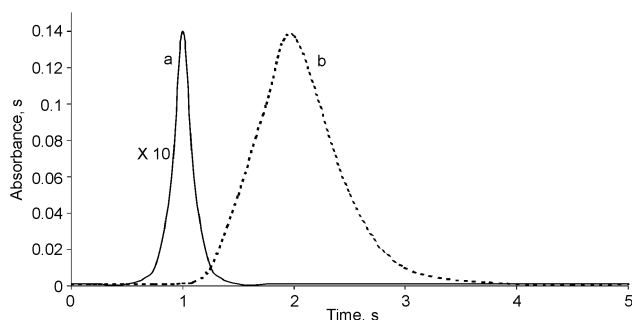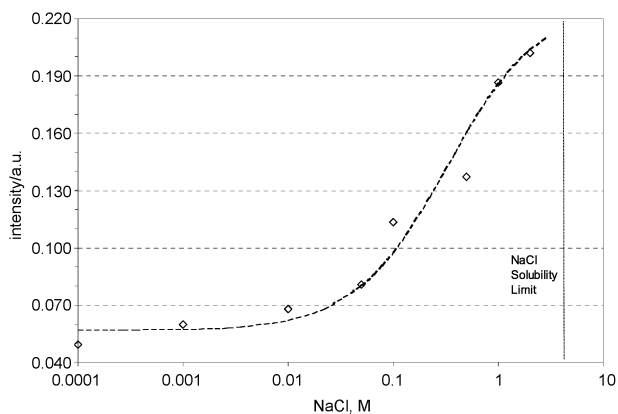
Fig. 2 Transient signals from 25 ng of TBT-Cl trapped at 300 °C on: (a) untreated graphite tube; (b) Ir treated graphite tube. (Reconstruction based on computer printout.)

Fig. 3 Theoretical and measured response as a function of chloride concentration in the sample solution. ◊, measured values; - - -, theoretical fit using eqn. 10.

Sn-containing species from the gas phase. From the best fit of the experimental data to eqn. 8, a value for K_1 of 0.32 M L^{-1} was obtained.

## Matrix optimization and suppression of TBT-Cl formation

The composition of the chloride matrix optimal for TBT-Cl formation was determined by comparing responses from solutions of both NaCl and HCl. Fig. 4 shows that a 2 M chloride ion concentration is sufficient to obtain the maximum conversion of TBT-OH to TBT-Cl, resulting in the maximum signal intensity. It is important to note that the optimum chloride concentration is the same, whether NaCl or HCl is the source. However, the signal intensity using HCl is significantly higher, likely as a consequence of suppression of the formation of hydroxide species in this medium (eqns. 1–3) with a concurrent enhancement in the concentration of the chloride species. Fig. 5 compares the effects of various halides on response, presumably giving rise to the formation of TBT-Cl, TBT-Br and TBT-I. The highest analytical signal was obtained using sodium iodide to promote TBT-I generation. The increased signal may be due to a higher volatility of TBT-I compared with TBT-Cl or TBT-Br, but the stability of the iodide species and its enhanced trapping efficiency may also play a role. For analytical proposes, because of ready availability, all further work was performed using chloride ions for the halide generation process. The nature of the bromide and iodide species requires further investigation.

Optimization of flow injection and trapping efficiency

Fig. 6 shows the effect of the argon purge gas flow rate on the analytical signal. It is evident that 150 ml min^{-1} is the minimum Ar gas flow rate for which the generated TBT-Cl is
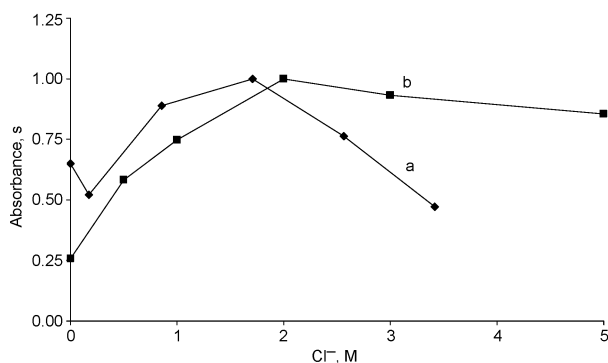
Fig. 4 Effect of chloride concentration and source of chloride on analytical response: a, 100 ppb TBT in NaCl; b, 20 ppb TBT in HCl.
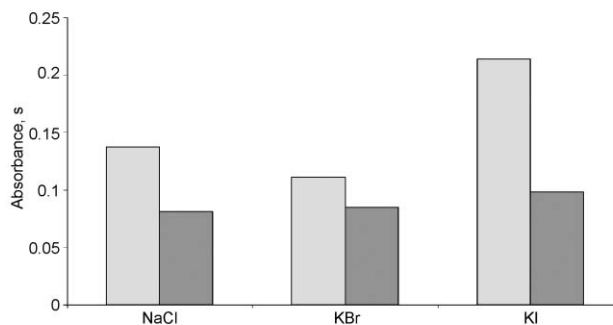
Fig. 5 Effect of halide counterion on response from 25 ng TBT: (☐) 0.5 M and (■) 0.05 M halide solutions.
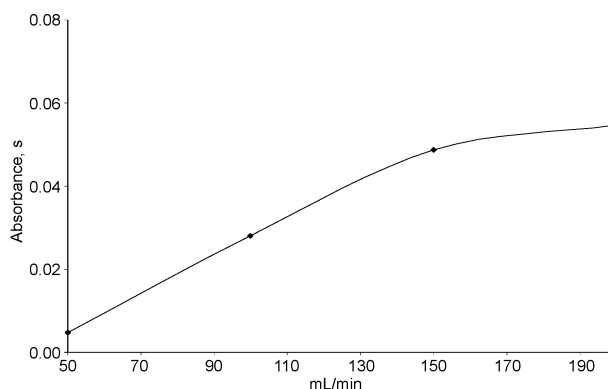
Fig. 6 Effect of argon flow rate on integrated response from TBT.

efficiently transported to the graphite tube when a solution carrier flow rate of 2 ml min^{-1} is used.

TBT-Cl generation and collection is unaffected by solution carrier flow rate and a value of 2 ml min^{-1} was thus used in this study to minimize the time required for replicate analyses. At higher carrier flow rates, the optimum Ar purge/transfer gas flow should be increased.

The overall efficiency for chloride generation, purging and trapping was estimated by processing a 5 ppb TBT solution for a 2 min generation time. The TBT content in the aqueous waste from the GLS was assessed, from which an efficiency of 40 ± 10% was calculated.

Analytical results

The selectivity of the method was assessed by examining the response from solutions spiked with 1 mg L^{-1} concentrations of inorganic tin, monobutyltin and dibutyltin. No response was obtained for any of these species, whereas tributyltin could be detected at the low ppb level.

The analytical blank was initially difficult to control because of condensation of the TBT-Cl along the length of the transfer line connecting the gas–liquid separator with the graphite furnace. Heating the transfer line to 65 °C decreased carryover from spiked samples, permitting a controlled, consistent, detectable blank to be measured. Contributions to TBT from plasticizers in the peristaltic pump tubing are surmised to be the most probable source.

An absolute detection limit of 1.3 ng TBT (as tin) was estimated from repetitive measurements of the blank. This corresponds to a detection limit of 0.33 ppb. The latter depends on the volume of sample processed, as illustrated by the data in Fig. 7, which shows analytical response to be linearly dependent on the sample volume processed. As a consequence of a well-controlled blank, the detection limit can be "tuned" to
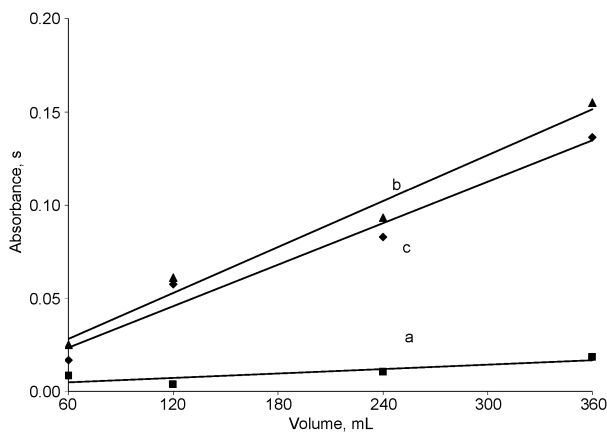
Fig. 7 Effect of sample volume on analytical response from TBT: a, reagent blank, b, 5 ppb TBT, and c, net signal.

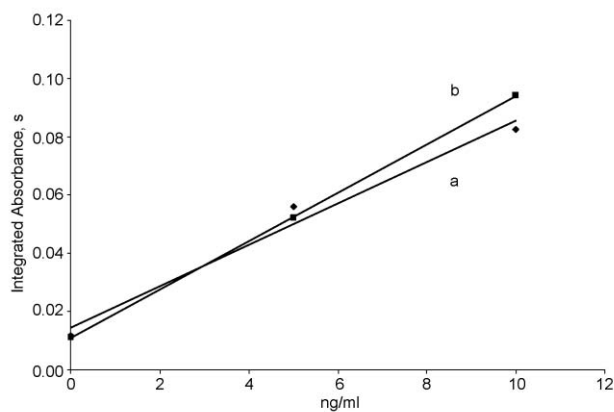**Fig. 8** Calibration curves prepared in: a, 2 M HCl, and b, 2 M HCl + 2.5% HAc.

Table 2 Figures of merit

LOD[a]/ ng ml^{-1}	LOQ[b]/ ng ml^{-1}	RSD[c] (%)	Sensitivity Abs./ng^{-1}
0.33	1.1	3.3	0.006

[a]Limit of detection (3σ). [b]Limit of quantification (10σ). [c]Relative standard deviation, $n = 4$, 2 ml, 5 ng ml^{-1} solution.

Table 3 Analytical results. All concentrations as μg TBT (as Sn) based on 1 g of sediment

Standard additions before leaching	Standard additions after leaching	External calibration	Certified value
1.13 ± 0.03[a]	1.02 ± 0.03[a]	1.27 ± 0.04[a]	0.98 ± 0.13[b]

[a]SD. [b]95% confidence interval.

the desired level to meet the analytical challenge. The relative detection limit lies in the sub-ppb range, as summarized by the data in Table 2.

Response is linear over 2 orders of magnitude of concentration, up to about 100 ng TBT (as tin). The method can thus accommodate both heavily polluted and relatively clean samples without changing the trapping conditions or volume of sample processed.

Three calibration approaches were compared for the quantitation of TBT in PACS-2 sediment extracts: standard additions, wherein the spikes were added before the microwave leaching of the sample; standard additions with calibration spikes added to the leachate after the microwave step; and the use of external calibration. Fig. 8 presents a comparison of the calibration curves generated from a simple 2 M HCl and a 2 M HCl + 2.5% (v/v) acetic acid solution. Acetic acid (HAc) extracts of the sediment cannot be analyzed directly without the addition of 2 M HCl because, as noted above, the measurement of TBT (as tin) requires favourable formation of TBT-Cl in the aqueous phase. To achieve optimum Cl$^-$ requirements and dynamic range for linear calibration, it was necessary to dilute the sediment leachate with 2 M HCl. The difference between the slopes of the two curves is approximately 10%, indicating that the matrix effect arising from the presence of HAc, compared to the pure 2 M HCl solution, was minimal. This permitted sediment extracts to be accommodated. Table 3 summarizes the results of this exercise; all three calibration approaches provided acceptable results compared with the certified value. The recovery of the TBT spike during the leaching process was found to be 104 ± 4%, indicating that no spike was lost or irreversibly adsorbed onto the sediment during the extraction process.

Conclusion

Development of a simple, robust and specific analytical system for trace element speciation is crucial for routine analytical practice. Flow injection vapour generation with *in-situ* trapping of analyte on a graphite furnace coupled with AAS detection represents such an approach for the determination of TBT in aqueous media. The system is easily assembled from readily available off-the-shelf components common to many laboratories and its operation does not require access to chromatography apparatus, which is not always available in a laboratory dedicated to trace element analysis. This approach should theoretically be useful for the determination of other organometallic pollutants, including methylmercury and methyl-arsenic species.

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