

SPECIATION OF NON-PESTICIDAL ORGANOTIN COMPOUNDS USING GAS CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Gallagher, P.A.¹, Cincinatti/US, Evans, O.¹, Cincinatti/US Park, A.N.², Cincinatti/US, Schwegel, C.A.¹, Cincinatti/US, Ackerman, A.H.³, Cincinatti/US, Creed, J.T.¹, Cincinatti/US, Wilbur, S.⁴, Seattle/US
 1. US EPA, National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, 26 W. Martin Luther King Dr., Cincinnati, OH 45268
 2. Oakridge Research Fellow; 3. Oakridge Postdoctoral Research Fellow; 4 Agilent Technologies

INTRODUCTION

Organotins are used as stabilizers in polyvinyl chloride (PVC) pipes and are broadly classified as endocrine disruptors. The use of PVC pipes within drinking water distribution systems is growing as old pipes are replaced and new service mains are installed. The installation of these pipes has generated a growing concern with respect to organotin exposures produced by the slow release of the stabilizer from the PVC pipe. In response to this the Office of Ground Water and Drinking Water (OGWDW) placed monomethyl tin (MMT), dimethyl tin (DMT), monobutyl tin (MBT) and dibutyl tin (DBT) on the 1998 Contaminant Candidate List (CCL). The CCL is used by the OGWDW to identify Contaminant which may possess

potential health risks to the public. Organotins are listed in the occurrence and research priority part of the CCL. This means occurrence, health, and treatment data and analytical methods are required prior to any regulatory decision making. The OGWDW is planning to collect occurrence data on organotins under a future Unregulated Contaminant Monitoring Rule (UCMR). This data collection process requires the analytical capability to determine organotin compounds in drinking water matrices. GC-ICP-MS is a promising approach to analyzing organotins at the low to sub-ppt concentration range. This evaluation is being conducted through a Cooperative Research and Development

Agreement (CRADA) between Agilent Technologies, Inc. and U.S. Environmental Protection Agency (EPA) National Exposure Research Laboratory (NERL). The initial focus of the CRADA is to evaluate the sensitivity and stability of the GC-ICP-MS interface and to evaluate the feasibility of utilizing this interface in a more routine laboratory setting. This poster presents data on:

- Reliability of Utilizing Xenon as an Instrument Tuning Gas
- Can Xenon be used as an Internal Standard for Tin?
- Day to Day Reproducibility
- Detection Limit Evaluation
- Isotope Ratio Precision

EXPERIMENTAL

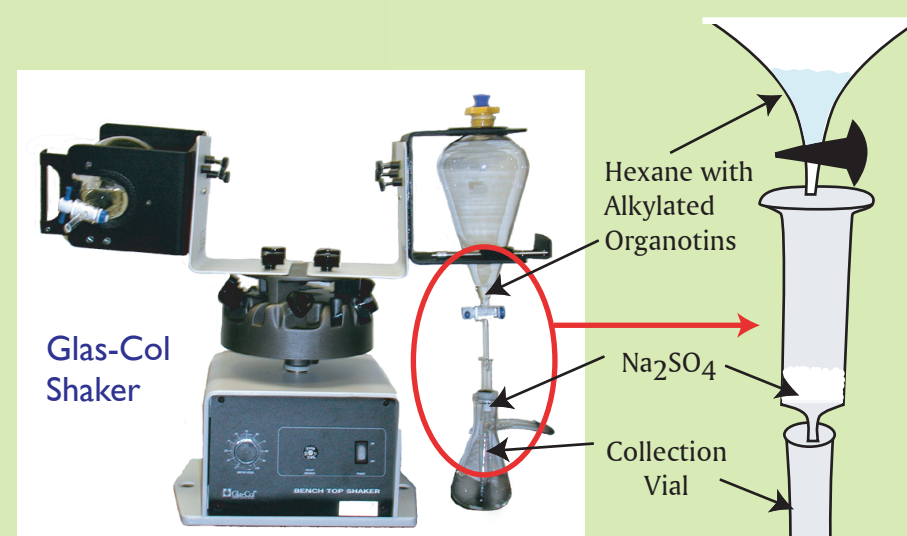
Analytical Procedure for Alkylation and Extraction

- Placed in Separatory Funnel
 - DDI or water sample (500 mL)
 - 10 mL 1M Acetate Buffer, pH 5.1
 - Mix
 - 1.0 mL Sodium Tetraethylborate (STEB)
 - 4mL Hexane
- Shaken for 30 minutes on Glas-Col Bench Top Shaker
- Aqueous and organic layers are allowed to separate for 30 minutes
- Discard aqueous layer
- Pass organic layer (Hexane) through Na₂SO₄ for drying and collect for analysis by GC-ICP-MS

(Scheme after Sadiki and Williams, etc., 1996)

Instrumentation

- Agilent 6890N Gas Chromatograph (GC) with Auto Sampler
- Agilent 7500A Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with Shield
- Glas-Col Bench Top Shaker



The organotin compounds were alkylated using STEB at a pH of 5.1 and extracted into hexane. The hexane was passed thru a drier tube and injected onto a DB-17 column from J & W Scientific. The column flowrate is 1.7 and the GC temperature setting is 55°C for 1 min then 30°C/min to 280°C with splitless injection. The alkylation/ extraction procedure was modeled after a method by Sadiki and Williams (Chemosphere, 1996). This procedure was used in this initial evaluation because it is currently used in the authors' laboratory to investigate GC-pulsed flame photometric detection of organotins.

Figure 1. System Diagram of the GC-ICP-MS

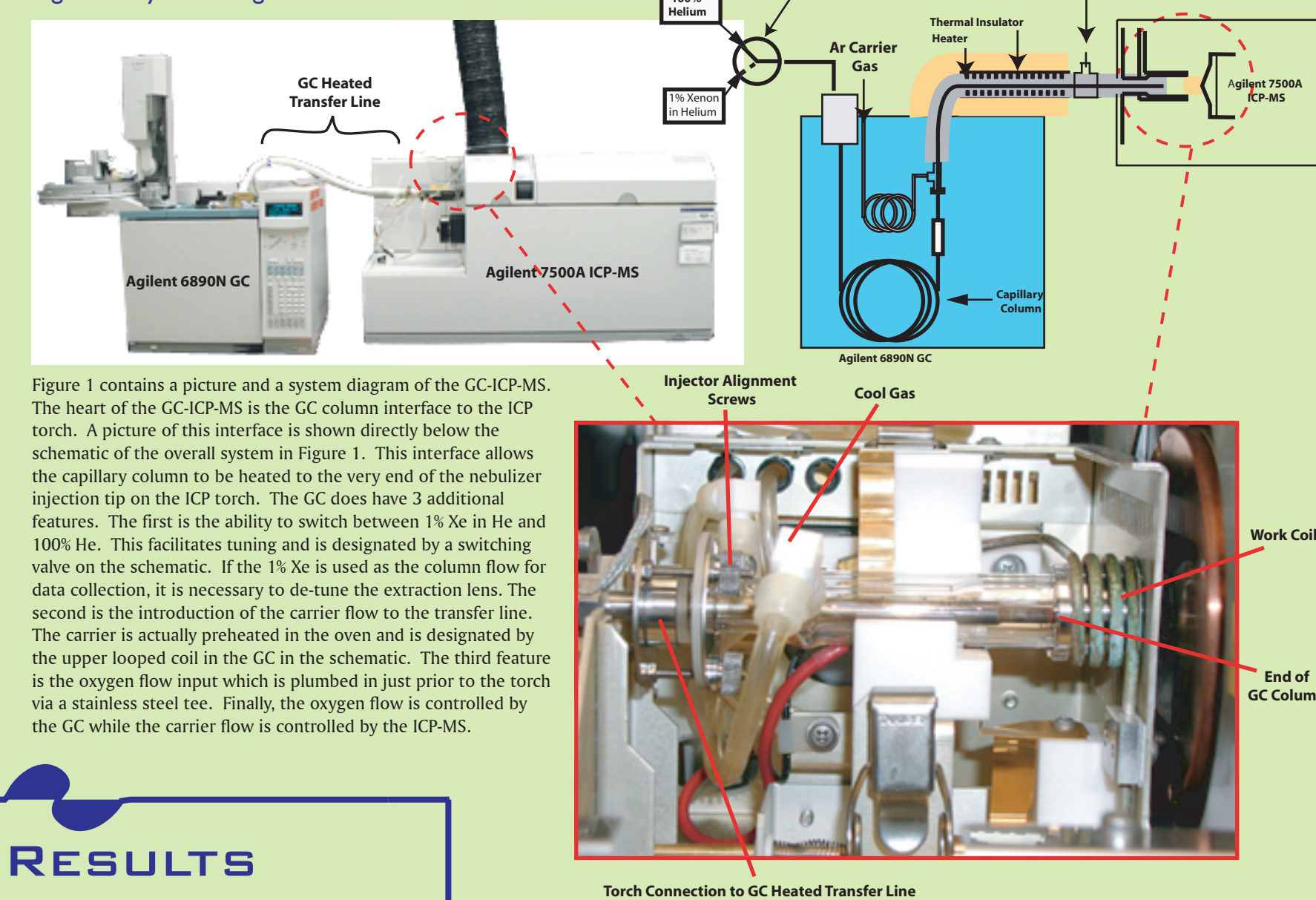


Figure 2 - 4. Reliability of Utilizing Xe as an Instrument Tuning Gas for GC-ICP-MS

The GC-ICP-MS interface poses a unique set of challenges in terms of the routine tuning of the ICP-MS for optimum Sn sensitivity. Part of this challenge is the Sn signal is entering the plasma in a column flow of 1-2 mL and the Sn GC signal is a transient with a duration of 2-4 seconds. These two conditions make the instrument virtually impossible to tune without a secondary tuning gas. The tuning gas recommended by Agilent Technologies, Inc. is a 1% Xe in He and is introduced to the plasma through the capillary column. A small switching valve facilitates the switching between 1% Xe (tuning) and 100% He (sample analysis). The question that arises is: "Does the Xenon signal provide a good indicator of the Sn signal during the ICP-MS tuning process?" An initial evaluation of the GC-ICP-MS system using Xe indicated that carrier flow, oxygen flow and torch position were the main instrumental parameters which influenced the sensitivity once a reasonable lens tuning was achieved. The word "reasonable" in the last sentence is used because a conventional solution nebulization tune produces a dismal signal for the GC interface. The ion lenses were not investigated as instrumental parameters because the transmission of Xe124 and Sn120 may be offset by a constant via an improved lens tuning. However, the lenses themselves should not preferentially transmit mass 124 vs 120 for any given lens tuning. The parameters chosen were conditions which may impact the plasma's ability to produce ions from Xe and Sn. These parameters were further paired down using Xe and looking for the parameters which produced the greatest change in signal intensity.

The first parameter investigated was carrier flowrate. The carrier is added through the transfer line between

the column and the 1/16 stainless steel tubing. (See Figure 1) This carrier in effect aids in pushing the 1-2 mL column flow towards the sampling cone. The data in Figure 2 was collected by monitoring both Sn and Xe during a sample injection. The DMT signal was integrated and the average from the Xe124 signal was determined during the elution of the DMT. The Xe and Sn were normalized independently using the largest signals obtained over the flow rate range investigated. The carrier flowrate profile indicate a relatively narrow window for optimal Sn signal around 0.43 L/min. The Xe profile is nearly superimposable on the Sn indicating the Xe is a good tuning gas for Sn (Similar carrier flowrate profiles were obtained for DBT, MMT and MBT). This type of data indicates that an autotune function may be applicable and this is extremely beneficial if this technology is to be used for routine analysis.

In Figure 3, the second parameter, oxygen flowrate, was investigated. The oxygen was added via a stainless steel tee less than 10cm from the back of the torch. In this configuration, these two parameters are difficult to optimize independently (i.e. hold the overall flowrate (carrier + oxygen) constant and only vary the percentage of oxygen in the overall flow.) Therefore, to evaluate the impact of oxygen on the signals the carrier was set to its optimum found in Figure 2. This point (0.43 L/min carrier) has been highlighted by the yellow line connecting Figure 2 and Figure 3. To the right of the yellow line, in Figure 3, the oxygen flow is increasing and so is the overall flow. The increase in Sn signal observed to the right of the yellow line would not be predicted based on increased overall flow alone (see Figure 2). This increase in Sn indicates the oxygen has a secondary means of

Figure 2. Effect of Carrier Gas Flowrate on Sn 120 and Xe 124

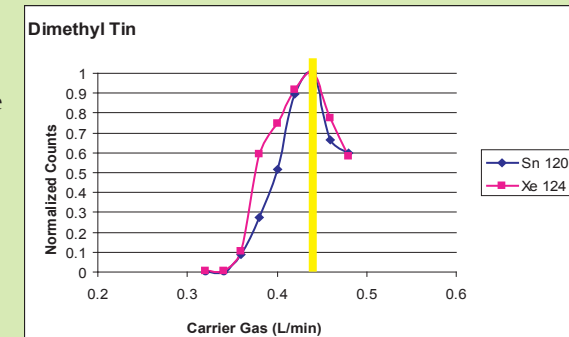
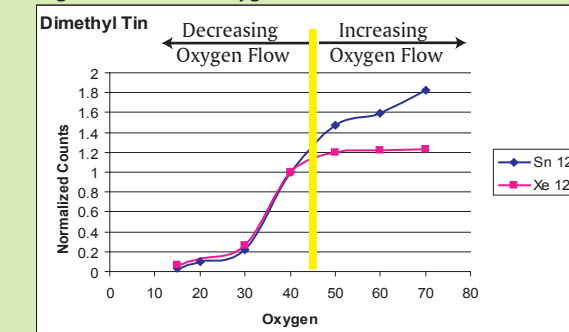


Figure 3. Effect of Oxygen Flowrate on Sn 120 and Xe 124



increasing the Sn signal. This same increase is not observed for the Xe signal. To the left of the yellow line the Sn and Xe signals are nearly co-linear, similar to Figure 2. More controlled studies will be required in order to understand this effect.

It is worth noting that the authors believe the actual profile may shift with different torch sampling depths etc., but it is likely that the Xe will track the Sn signal. Therefore, these initial studies indicate that Xe is an acceptable tuning gas for carrier flowrate adjustment.

Figure 4. Effect of Torch Position on the Xe and Sn Response

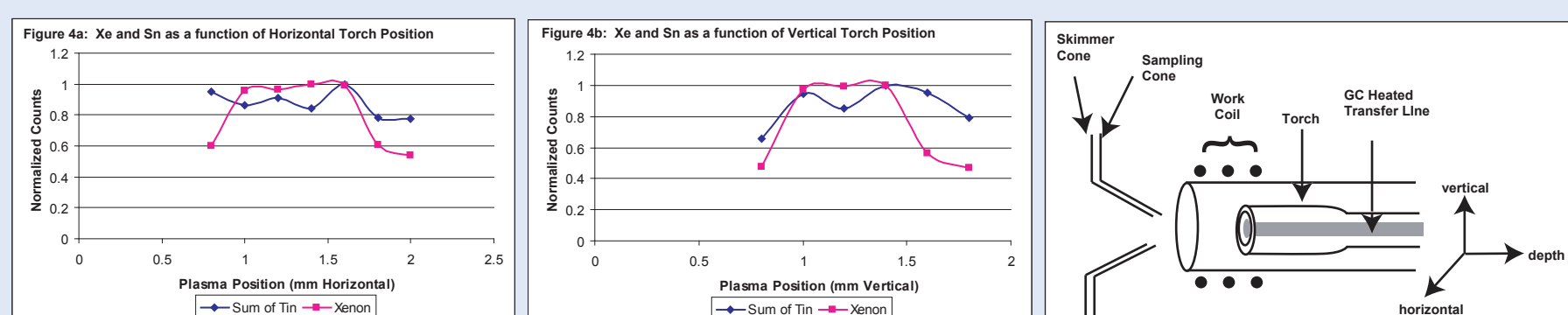


Figure 4 investigates the effect of torch position (horizontal and vertical) on the Xe and Sn signals. Torch position was chosen as a parameter because 0.2 mm changes in the torch position would result in a 50% change in the Xe signal during a manual tune. In this case, the Xe tune gas is indicating that torch positions near these sharp signal gradients will produce poor sensitivity and stability for Xe and in turn Sn.

The question here is "Does Sn have a similar torch position profile and can Xe be used to find the optimum Sn signal?"

The torch position data was collected by using the 1% Xe as the column flow and making an injection of organotins at each torch position. The Xe signal was

averaged and the Sn peaks integrated for each torch position. The Xe and Sn signals were then normalized based on the highest signal observed. Figure 4a is a response profile for Xe and Sn as a function of horizontal torch position at a fixed vertical torch position of 1.2 mm. The Xe signal is stable from 1.0 to 1.6 mm and drops off by 40% on both sides with just a 0.2 mm change. The Sn signal in Figure 4a does not produce the same sharp increase in response when the torch position is changed from 0.8 mm to 1.0 mm and 1.6 mm to 1.8 mm. Therefore, optimal Xe signals are observed over a narrower horizontal torch position range than Sn but a 0.5 mm plateau is observed for both Xe and Sn. The effect of vertical torch position on Sn and Xe is investigated in Figure 4b with a fixed horizontal position of 1.4 mm. The vertical profile is similar to

the horizontal in that the Xe signal sharply increases with a 0.2 mm change and then remains relatively constant until it drops off on the other side of the plasma. The change in Sn signal is not as pronounced over any 0.2 mm change and is relatively constant from 1.0 to 1.5 mm. The resulting "plateau region" is smaller for GC-ICP-MS (relative to solution nebulization) and the optimum Xe signal is found in a smaller cross sectional area of the plasma than Sn. The net effect is that from a torch position perspective, a stable Xe tune may be more difficult to achieve than a stable Sn tune. Therefore, based on this initial data, a 1% Xe gas is an effective means of optimizing the torch position and may lend itself to an autotune function which is beneficial in a routine laboratory setting.

Figure 5. Can Xenon be Used as an Internal Standard

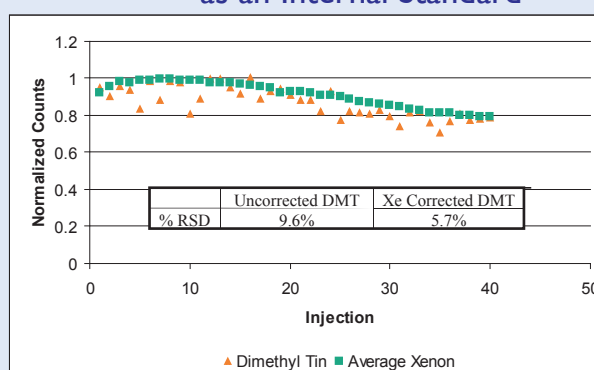


Figure 2 - 4 indicate that 1% Xe is an effective means for optimizing carrier flow, oxygen flow and torch position. This combined data indicates that Xe may be able to be used as an instrument drift standard. Figure 5 investigates the use of Xe as an instrument drift standard for Sn. The data in Figure 5 was collected by using the 1% Xe gas for the column flow and programming the instrument to inject a standard 40 times. This represents approximately 10 hours of analysis. The organotin peaks were integrated and the Xe signal was averaged for each injection. The Xe and DMT signals were independently normalized and plotted in Figure 5. The correlation between Xe (■)

and DMT (▲) is difficult to assess in Figure 5 given the variation in integrated DMT signal. In order to evaluate this data, the Xe signal was used as an "internal standard" for the DMT and a % RSD was calculated for both uncorrected DMT and Xe corrected DMT which are reported as a table inset in Figure 5. The Xe corrected data reduces the % RSD from 9.6% to 5.7% for DMT. Similar reductions in % RSD were observed for MMT, MBT and DBT. This reduction indicates that the Xe signal drifts with the Sn signal. This preliminary data provides additional credence to the use of Xe as a tune gas and opens up the potential to use Xe as an internal standard.

Table 1. Day to Day Instrument Stability: Standard Reproducibility on 3 Non-Consecutive Days

	MMT ¹ ($\bar{x} \pm 2\sigma$) $\times 10^4$	DMT ¹ ($\bar{x} \pm 2\sigma$) $\times 10^5$	MBT ² ($\bar{x} \pm 2\sigma$) $\times 10^3$	DBT ² ($\bar{x} \pm 2\sigma$) $\times 10^4$
Day 1 n=5	3.53 ± 0.28	1.43 ± 0.11	8.27 ± 0.46	1.10 ± 0.07
Day 4 n=3	3.57 ± 0.30	1.45 ± 0.16	7.68 ± 1.86	1.00 ± 0.23
Day 5 n=5	3.69 ± 0.66	1.52 ± 0.25	8.85 ± 2.12	1.16 ± 0.24
Pooling of Data from 3 Non-Consecutive Days n=11	3.58 ± 0.39	1.46 ± 0.17	8.27 ± 1.58	1.09 ± 0.20
% RSD ON Non-Consecutive Days n=11	5.47%	5.76%	9.53%	9.13%

1. 10 ppb MMT and DMT mix 2. 1 ppb MBT and DBT mix

Figure 2 - 4 evaluates the use of Xe as a tune gas for GC-ICP-MS. This type of data provides a basis for describing a procedure which can be used by a routine laboratory to tune the instrument. Ideally, this would be incorporated into an autotune feature. A second characteristic in evaluating an instrument for a routine application is day to day reproducibility of a mid range standard. Table 1 summarizes the reproducibility for a 10 ppb standard of MMT and DMT and a 1 ppb standard for MBT and DBT on 3 non-consecutive days. The data was collected using the same tune file for all 3 days. The average integrated count rate and a 2σ control limit is calculated for each compound for each day. These concentrations would represent 200 ppt and 20 ppt in the water sample. A comparison of the day to day averages and control limits indicate very little instrument response change. In fact, using the control limits calculated for each compound on day 1, most of the data for day 4 and day 5 would be within these control limits.

In the second to last row the data is pooled across days and the 2σ control limits are calculated. These results are comparable to any of the single day results. Finally, in the last row of Table 1 reports a multiple day %RSD. For MMT and DMT, the multiple day %RSD is less than 6% while MBT and DBT are less than 10%. This indicates that the instrument can be run on 3 non-consecutive days and produce stabilities which are < 10% RSDs. Finally, this data indicates the instruments capability to be used in a more routine analytical setting.

Figure 6. Detection Limit Estimation for the GC-ICP-MS

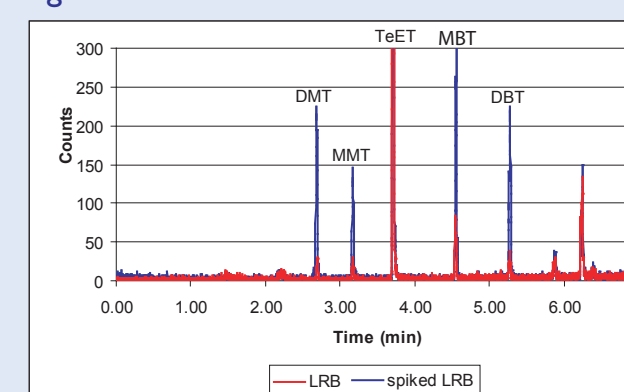


Figure 6 contains a chromatogram of the laboratory reagent blank (red). The chromatogram clearly indicates that detectable quantities of DMT, MMT, MBT and DBT are present. In an attempt to minimize the blank the following experiment / procedures have been utilized:

- Experiments using various quantities of STEB have indicated that the peak at 3.71 min [tetraethyl tin (TeEt)] is an impurity from the STEB.
- Experiments which involve pre-extracting the buffer, Na₂SO₄ and glass frits have produced a slight reduction in the contamination.
- All glassware is rinsed in DDI and muffled at 400°C after each use.
- The stop cocks and stoppers used in the separatory funnels are rinsed in hexane after each use.

Even with these procedures in place the LRB still contains detectable quantities of organotins. In order to estimate the detection limit a LRB was spiked with each of the organotins. The chromatogram of the spiked LRB is overlaid with the LRB in Figure 6. The 33 - 44 ppt spike produces a change in peak height of approximately 116 - 180 counts. The estimated detection limit is calculated to be 2 ppt based on 3 times the standard deviation of the noise. These estimated detection limits are in line with the requirements that the OGWDW is predicting are necessary for the detection of organotins under future occurrence studies.

Isotope Ratio Precision

One of the advantages of utilizing ICP-MS detection for organotin analysis is the possibility of utilizing isotope dilution to validate the procedure. The precision of the isotope ratio ultimately limits the precision of the isotope dilution analysis; therefore, isotope ratio precision was included in this preliminary evaluation of the GC-ICP-MS. Isotope ratio precision was

determined using a 3 ppb solution of MMT, DMT, MBT and DBT. The Sn masses chosen were 120 and 118 and the dwell time was set to 0.1 sec. Ten replicate injections of the standard were made producing %RSDs of less than 1.5%. These results indicate that enriched isotopic material would be beneficial for method validation purposes.

CONCLUSIONS

- The use of a 1% Xe tuning gas is an effective means of optimizing carrier flow and torch position for organotin analysis by GC-ICP-MS.
- The 1% Xe tuning gas can be used for the optimization of oxygen flow but its correlation to Sn response is not absolute. More controlled studies are required.
- Preliminary data indicates that Xe can be used as an instrument drift standard. This may, at a minimum, aid in documenting long-term instrument response differences.
- The ability to use 1% Xe as a tune gas and the ability to produce multiple day RSDs of less than 10% make GC-ICP-MS an analytical technique, which may be applicable to a routine laboratory setting.
- The estimated detection limits achievable with GC-ICP-MS are in the concentration range required for an occurrence study with the OGWDW.
- Isotope ratio precision of less than 2% will allow for method validation via isotope dilution analysis.



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