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**ORTEP STABILIZER TASK FORCE (STF) ANALYTICAL METHOD -
TOTAL TIN ANALYSIS OF ORGANOTIN STABILIZERS IN WATER**

SUMMARY

Water samples containing mono- and dialkyl (methyl, butyl, or octyl) tin stabilizers are digested with acetic acid, heated to approximately 60°C, and analyzed using inductively coupled plasma-mass spectrometry (ICP-MS).

GENERAL INFORMATION

--Reagents may contain organotin impurities. It is essential to verify the purity of reagents before use and monitor contamination by analyzing reagent blanks with each analytical batch.

--This procedure is not suitable for analyzing mixtures of the individual test substances. Due to the total tin analysis, specificity between test substances with different alkyltin moieties (i.e., methyl vs. butyl) and degrees of alkylation (i.e., mono- vs. di-) is not possible.

--During method validation, it was determined that the method described in this report was not suitable for the determination of several tri- or tetraalkyltin compounds in water, specifically tributyltin chloride, trioctyltin chloride, tetrabutyltin, and tetraoctyltin.

I. Reagents and Solutions

A. Chemicals

Acetic acid, CH₃COOH (glacial), ultra-high purity (re-distilled), 99.99% +

Reagent water, Milli-Q or equivalent purity

Methyltin tris(2-ethylhexylmercaptoacetate) [MMT(2-EHMA)], CH₃Sn(C₁₀H₂₀O₂S)₃

Dimethyltin bis(2-ethylhexylmercaptoacetate) [DMT(2-EHMA)], (CH₃)₂Sn(C₁₀H₂₀O₂S)₂

Butyltin tris(2-ethylhexylmercaptoacetate) [MBT(2-EHMA)], C₄H₉Sn(C₁₀H₂₀O₂S)₃

Dibutyltin bis(2-ethylhexylmercaptoacetate) [DBT(2-EHMA)], (C₄H₉)₂Sn(C₁₀H₂₀O₂S)₂

Octyltin tris(2-ethylhexylmercaptoacetate) [MOT(2-EHMA)], C₈H₁₇Sn(C₁₀H₂₀O₂S)₃

Dioctyltin bis(2-ethylhexylmercaptoacetate) [DOT(2-EHMA)], (C₈H₁₇)₂Sn(C₁₀H₂₀O₂S)₂

Inorganic Tin (Sn) standard solution (calibration standard)

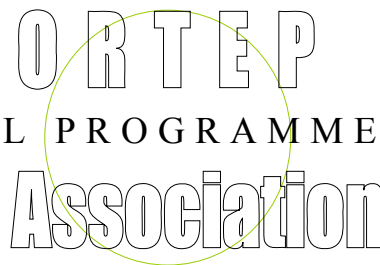
Inorganic Rhodium (Rh) standard solution (internal standard)

B. Prepared Reagents and Solutions

1. Stock Solution A (Analytical Standard Solution): Obtain an ultra-high purity (99.99% +) commercial inorganic tin standard stock solution (e.g., Merck No. 170242, 1000 mg/L). If using the actual test substance to prepare an analytical standard solution, dissolve the test substance in a small amount of methanol, bring to volume with methanol, and homogenize.

NOTE: Depending on the sample matrix, calibration solutions may be prepared

ORGANOTIN ENVIRONMENTAL PROGRAMME



using the actual test substance itself, rather than inorganic tin. During method validation, when analyses of the test substances were conducted in OECD ecotoxicity medium, it was observed that the response of the ICP-MS instrument was different for the actual test substance versus inorganic tin, due to the influence of the ions present in the sample matrix.

2. Stock Solution B (Internal Standard): Obtain an ultra-high purity (99.99% +) commercial rhodium standard stock solution (e.g., CPI International No. 4400-1000442, 1000 mg/L).

C. QA/QC Samples

1. Calibration Solutions: A minimum of five (5) calibration solutions in the appropriate concentration range (not including zero) should be prepared by diluting the corresponding inorganic tin or test substance stock solution with reagent water. To each calibration solution, an aliquot of internal standard solution should be added. Calibration solutions should be prepared fresh for each day of analysis.
2. Method (Laboratory) Blank: For each analytical batch, prepare a method blank of reagent water at the same volume as the samples being analyzed.
3. Matrix Spike: For each analytical batch, prepare a matrix spike using the appropriate volume of actual sample. Spike the sample with the compound of interest at the approximate mid-point of the calibration curve. A laboratory control spike (LCS) or “blank spike” can also be prepared using the same procedure, only using reagent water instead of actual sample.
4. Duplicate: For each analytical batch, prepare an analytical duplicate sample using the appropriate volume of actual sample.

II. Apparatus

A. Thermostated water bath

Inductively coupled plasma-mass spectrometer

Argon gas supply (99.99% purity)

125 mL Polycarbonate bottles

Transfer pipettes (disposable)

Volumetric flasks (varied volumes)

Volumetric pipettes (varied volumes)

- ### B. Glassware
- Use of PTFE, polycarbonate, or some form of disposable plastic containers/apparatus is preferred, as methyltins have been known to sorb to glass. Prior to using plastic containers however, verification that they do not leach tin at levels greater than the analytical detection limits should be performed.

Cleaning of non-disposable apparatus should be performed after each analysis, and should include washing with a laboratory cleaner (e.g., Alconox™), followed by repeated

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Association

rinsing with reagent water, acetone, and hexane prior to initiation of the next round of analyses. Examination of all non-disposable glassware for cross-contamination should be conducted frequently. If a batch of glassware is suspected of contamination due to exposure to high organotin concentrations, it is advisable to acid-rinse all glassware with high purity, 10 N nitric acid or equivalent. Acid rinsing removes even ultra-trace quantities of organotins adhering to glass surfaces.

III. Sample Preparation

1. Water samples should be kept in 1-L amber glass or opaque PTFE/polycarbonate/plastic bottles with PTFE-lined caps and stored at 4°C for a holding time of no more than 24 hours. Samples should be frozen if storage is to be prolonged. Holding time studies may be performed to evaluate this issue further.
2. Use the appropriate volume of sample for the expected analytical range; measure and note the volume of sample extracted in order to calculate the final results. Method validation samples were prepared using 25 mL sample volume for analyte concentrations 15–4,500 µg Sn/L. Prepare required QC samples as appropriate (i.e., calibration standards, method blank, matrix spike, analytical duplicate – see Section I.C.).
3. Transfer all samples, blanks, QC spikes, and reference standards to the appropriate sample container and treat each as follows:
 - a) Add 50 mL of acetic acid (~100%).
 - b) Heat the samples in a water bath at approximately 60°C, for at least 1 hour.
 - c) Add a known calculated amount of the internal standard rhodium solution prior to analysis.

V. Analysis

Set up and operate the instrument with the proper operating parameters according to the instrument manufacturer's instructions. Allow at least 30 minutes for the instrument to equilibrate, prior to analyzing any samples. During the method validation study, the following equipment and conditions were used:

Instrument:	PerkinElmer SCIEX Elan DRC II
Software:	Elan version 2.4
Autosampler:	Cetac ASX-510
Readings/repeat:	1
Repeats:	3
Mass isotopes measured:	Tin m/z = 116, 118, <u>120</u> (underlined mass used for quantitation)
Sweeps/reading:	20



 ORGANOTIN ENVIRONMENTAL PROGRAMME

Dwell time: 50.0 ms
 Read delay: 15 s
 Scan mode: Peak hopping
 Mass isotope internal standard: Rhodium m/z = 103

The test substance content in the sample is determined by analysis of the tin concentration using ICP-MS at a mass of 120, including the internal standard rhodium (mass 103). The tin concentration is also determined at the alternative mass 118. The difference between the concentrations at the two masses should be less than 10%.

Quantitation is conducted using the graph constructed from the calibration solutions [intensity (ratio peak height tin/peak height internal standard) vs. concentration]. Instrument linearity should be demonstrated for the five (minimum) calibration solutions (excluding zero) using linear regression. The correlation coefficient of the calibration curve constructed from the detector response (counts/second) vs. concentration of the standard solutions, should be at least 0.99. The achieved limit of detection (LOD) and limit of quantitation (LOQ) are defined as respectively three times and ten times the standard deviation of the measured test substance concentration in the blank validation samples (i.e., the LOD was determined using the background noise of the detector).

VI. Calculations

1. The quantitative values shall be reported in appropriate units, such as micrograms of tin per liter ($\mu\text{g Sn/L}$) for aqueous samples.
2. If dilutions are performed, the appropriate corrections must be applied to the sample values.
3. Measured tin concentrations are converted to estimated test substance concentrations by applying a multiplication factor calculated from the ratio of the molecular weights of tin and the individual test substances (see Table 1).

Table 1. Total Sn to Test Substance Multiplication Factors

Test Substance	Molecular Weight (g/mol)	Molecular Weight - Sn (g/mol)	Multiplication Factor
MMT(2-EHMA)	743.7		6.265
DMT(2-EHMA)	555.4		4.679
MBT(2-EHMA)	785.6	118.7	6.618
DBT(2-EHMA)	639.6		5.388
MOT(2-EHMA)	841.9		7.093
DOT(2-EHMA)	751.8		6.334

ORGANOTIN ENVIRONMENTAL PROGRAMME
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VII. REFERENCES

- de Haan, H.P.M. and de Wolf, J.M. 2005. Validation of the analysis of: Monomethyltin tris(2-ethylhexylmercaptoacetate) (CASRN 57583-34-3), Dimethyltin bis(2-ethylhexylmercaptoacetate) (CASRN 57583-35-4), Monobutyltin tris(2-ethylhexylmercaptoacetate) (CASRN 26864-37-9), Dibutyltin bis(2-ethylhexylmercaptoacetate) (CASRN 10584-98-2), Monooctyltin tris(2-ethylhexylmercaptoacetate) (CASRN 27107-89-7), and Dioctyltin bis(2-ethylhexylmercaptoacetate) (CASRN 15571-58-1) in water using ICP-MS (total tin analysis). TNO Report V5160. Study conducted by TNO Quality of Life, Analytical Services for the ORTEP Association Stabilizer Task Force. Zeist, The Netherlands.
- USEPA. 1998. Method 6020A, Inductively Coupled Plasma – Mass Spectrometry. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Draft Update IVA. January 1998.



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APPENDIX A

A summary of the method validation results of MMT(2-EHMA), DMT(2-EHMA), MBT(2-EHMA), DBT(2-EHMA), MOT(2-EHMA), and DOT(2-EHMA) in ISO and OECD ecotoxicity media is presented in table A.1 (de Haan and de Wolf 2005).

Table A.1 Summary total tin method validation results in ecotoxicity media.

Test Substance	Fortification	ISO Medium		OECD Medium	
	Level ($\mu\text{g Sn/L}$)	Mean Recovery (%)	RSD (%)	Mean Recovery (%)	RSD (%)
	LOD	--	0.6 $\mu\text{g Sn/L}$	--	1.4 $\mu\text{g Sn/L}$
	LOQ	--	2.1 $\mu\text{g Sn/L}$	--	4.5 $\mu\text{g Sn/L}$
MMT(2-EHMA)	17.23	108	4.3	83	9.5
	52.27	95	1.2	103	1.8
	335.3	103	1.5	103	5.2
	5296	91	12	106	3.5
DMT(2-EHMA)	17.95	91	5.2	95	20
	55.03	83	9.3	100	8.2
	379.3	91	0.9	110	1.6
	5723	85	1.0	108	2.5
MBT(2-EHMA)	14.86	107	21	90	7.3
	45.23	105	3.3	110	3.1
	301.6	117	1.6	108	3.4
	4646	107	7.9	103	3.3
DBT(2-EHMA)	17.01	94	3.3	101	8.8
	54.30	81	11	104	9.4
	333.2	92	1.8	114	0.7
	5241	91	1.1	108	0.9
MOT(2-EHMA)	14.87	108	19	79	10
	44.62	92	17	97	7.8
	297.5	108	16	105	1.2
	4919	105	12	103	1.7
DOT(2-EHMA)	16.71	101	14	92	20
	50.71	89	13	99	12
	321.2	101	18	110	6
	5036	109	12	116	11