Determination of Organotin Compounds in Toy Materials by Agilent 5977A GC/MSD to Meet European Regulation EN71-3: 2013, Migration of Certain Elements

Application Note

Consumer Products, Materials

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Abstract

The EU approved Directive 2009/48/EC bans certain organotin compounds in toy material for public safety. This application note used the Agilent 5977A Series GC/MSD system to analyze 11 organotin compounds with excellent sensitivity and linearity. Additionally, good reproducibility and recovery were achieved through the analysis of three categories of toy materials. The 5977A Series GC/MSD provides a complete instrument solution to meet European regulation EN71-3: 2013.

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Introduction

Organotin compounds are chemical compounds based on tin with hydrocarbon substitutions. They are used in the toy industry as disinfectants due to their antibacterial and fungicidal properties. The triorganotin compounds are very toxic, and partly degrade to di- and monoalkyltin derivatives. These compounds may have a harmful effect on living beings, and can disrupt the normal growth of children. Due to their toxicity, certain organotin compounds have been banned or severely restricted for health or environmental reasons.

The EU Toy Safety Directive (2009/48/EC) seeks to ensure the safety of children by minimizing their exposure to potentially hazardous or toxic toy products. The European Standard on the safety of toys (EN71) supports the requirements of EU Directive 2009/48/EC, and Part 3 of the standard (EN71-3) covers the migration of certain elements from various categories of toy products. The most recent (2013) revision of EN71-3 has been published, supporting the new chemical requirements of the EU Toys Safety Directive, which take effect from 20 July 2013.

Toy materials and parts of toys are divided into three categories:

- **Category I:** Dry, brittle, powder-like, or pliable materials
- **Category II:** Liquid or sticky materials
- **Category III:** Coatings and scraped-off materials

EN71-3 specifies migration limits for 17 elements: aluminum, antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, strontium, tin (and organic tin compounds), and zinc. There are two migration limits for tin and organic tin specified for each category (Table 1). Toy materials in Category II (liquid products that may easily be swallowed) must meet the lowest limit of 0.2 mg/kg for total amount of organic tin compounds. The sample preparation method specified in EN71-3 (Figure 1) applies a total dilution factor of 20x. This means that the detection limit of a single organic tin compound in the samples as measured is 1 ppb; therefore, this application needs a very sensitive method for organic tin.

The Agilent 5977A Series GC/MSD has an extractor ion source, which provides greater ion throughput, higher abundance signals, and better sensitivity. This application note describes a method of determining organic tin compounds at the low level required in three categories toy materials. Calibration, limit-of-detection (LOD), reproducibility, and sample spike recovery are addressed.

Table 1. Categories of Toy Materials and the Respective Migration Limits of Tin and Organic Tin

Toy material	Category 1	Category 2	Category 3
Coatings of paints, varnishes, lacquers, printing inks, polymers, foams and similar coatings			✓
Polymeric and similar materials, including laminates, whether textile reinforced or not, but excluding other textiles			✓
Paper and paper board			✓
Textiles, whether natural or synthetic			✓
Glass, ceramic, metallic materials			✓
Other materials whether mass colored or not			✓
Compressed paint tablets, materials intended to leave a trace or similar materials in solid form appearing as such in the toy	✓		
Pliable modeling materials, including modeling clays and plaster	✓		
Liquid paints, including finger paints, varnishes, lacquers, liquid ink in pens and similar materials in liquid form appearing as such in the toy		✓	
Glue sticks		✓	
Migration limits from toy materials (mg/kg)			
Tin	15,000	3,750	180,000
Organic tin	0.9	0.2	12

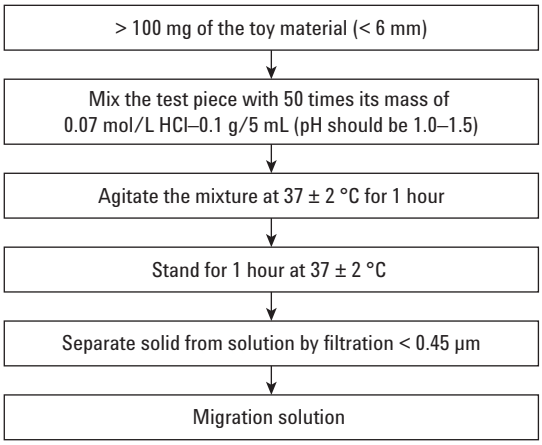

Figure 1. Sample migration flow.

Experimental

Reagents

The organic tin chloride compounds listed in Table 2 were purchased from Dr. Ehrenstorfer, Augsburg, Germany. Tributyl-d27-tin chloride, tetrabutyl-d36-tin, and triphenyl-d15-tin chloride were used as the internal standards (IS).

Stock Solution A: Weigh the specified amount (Table 2), to the nearest 0.1 mg, of the organic tin chloride into a 100-mL volumetric flask, and dissolve with methanol to prepare the 1,000 mg/L organic tin stock solution. (The solution is stable for up to 1 year when stored in the dark at 4 °C.)

Working Solution B*: Dilute stock Solution A 100 times with methanol to prepare the 10 mg/L organic tin working solution.

* If the method needs a lower LOD, make 1 mg/L working Solution B instead.

IS stock Solution C: Weigh 100 mg of Tributyl-d27-tin chloride, 100 mg of tetrabutyl-d36-tin, and 100 mg of Triphenyl-d15-tin chloride, to the nearest 0.1 mg, into a 100-mL volumetric flask, and dissolve with methanol to prepare the 1,000 mg/L IS mix stock solution. (The solution is stable for up to 1 year when stored in the dark at 4 °C.)

IS working Solution D: Pipette 0.2 mL of the IS stock Solution C into a 100-mL volumetric flask. Adjust to the mark with methanol to prepare the 2 mg/L IS working solution.

Hydrochloric acid solution: Add 5.8 mL of 37 % hydrochloric acid and 250 mL of water to a 500-mL volumetric flask. Adjust to the mark with water to prepare the 0.07 ± 0.005 mol/L HCl solution.

Acetate buffer solution: Dissolve 16.6 g sodium acetate with 250 mL of water into a 500-mL volumetric flask. Add 1.2 mL of glacial acetic acid to reach a pH of 5.4 and adjust to the mark with water.

Derivatization agent (2 % mass concentration): Weigh approximately 200 mg of sodium tetraethylborate into a 10-mL volumetric flask, and adjust to the mark with water. (This solution is not stable, and must be prepared daily.)

Table 2. Required Weighed Portions of Organic Tin Compounds, and Their Weighing Factors, Corresponding to 100 mg of Organic Tin Cations (Expressed as Tributyltin Cation)

Substance (OTClx)	CAS#	Weighed portion (mg)	MW OTClx	MW OC	Weighing factor*	Relative MW
Dimethyltin dichloride	753-73-1	75.8	219.7	148.7	0.677	1.948
Methyltin trichloride	993-16-8	82.8	240.1	133.7	0.557	2.167
Di-*n*-propyltin dichloride	867-36-7	94.2	273.6	202.7	0.743	1.429
Butyltin trichloride	1118-46-3	97.4	282.2	175.8	0.623	1.648
Dibutyltin dichloride	683-18-1	104.7	303.6	232.7	0.767	1.245
Tributyltin chloride	1461-22-9	112.2	325.2	289.7	0.891	1.000
n-octyltin trichloride	3091-25-6	116.6	338.1	231.7	0.686	1.250
Di-*n*-octyltin dichloride	3542-36-7	143.4	415.6	344.7	0.830	0.840
Tetrabutyltin	1461-25-2	119.6	346.7	346.7	1.000	0.836
Diphenyltin dichloride	1135-99-5	118.6	343.6	272.7	0.794	1.062
Triphenyltin chloride	639-58-7	138.0	385.2	349.7	0.875	0.828

*Weighing factor = molar mass (organic tin cation)/molar mass (organic tin chloride)

Sample migration and derivatization procedure

The sample preparation procedure is given in Figure 1. The procedure follows EN71-3, which simulates gastric digestion as would occur in the case when a child swallows toy material.

Pipette 5 mL of the above migration solution to a 22-mL glass tube. Then add 0.1 mL of IS Solution D and 5 mL acetate buffer solution to adjust the pH to 4.7. Subsequently, add 0.5 mL of 2% sodium tetraethylborate and 2 mL of hexane. Vortex for 30 minutes and allow to stand until the phase separation is complete. The hexane fraction is then ready to be analyzed by GC/MS.

Calibration standards

Insert 5.0 mL of 0.07 mol/L HCl into each of seven 22-mL glass tubes. Then pipette 0, 20 µL, 50 µL, 100 µL, 0.2 mL, 0.5 mL, and 1.5 mL of working solution B, respectively. Add 0.1 mL of IS working solution D and 5 mL of acetate buffer solution to adjust the pH to 4.7. Then add 0.5 mL of 2 % sodium tetraethylborate and 2 mL of hexane. Vortex the mixture for 30 minutes and allow to stand until the phase separation is complete. Then, analyze the hexane fraction by GC/MS.

Instrumentation

The experiments are performed on an Agilent 7890B Gas Chromatograph System with split/splitless capillary inlet, an Agilent 5977A Series Mass Spectrometer with Extractor Ion source, and an Agilent 7697A Automatic Liquid Sampler equipped with a 10-µL syringe. The instrumental configuration and analytical conditions are summarized in Table 3. Table 4 presents the selected target ion and three qualifying ions for SIM method.

Table 3. Gas Chromatograph and Mass Spectrometer Conditions

GC conditions	
Column	Agilent J&W DB-5ms Ultra Inert capillary column, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
Injection volume	2 µL
Injection mode	Pulsed splitless, 25 psi until 0.75 minutes
Inlet temperature	275 °C
Carrier gas	Helium, constant flow, 1.0 mL/min
Oven program	50 °C for 1 minute, 20 °C/min to 280 °C, 280 °C hold 1 minute
Post run	300 °C for 2 minutes
MS conditions	
Solvent delay	3 minutes
Source temperature	250 °C
Quadrupole temperature	150 °C
Transfer line temperature	280 °C
EM gain factor	1
Mass mode	SIM

Table 4. Retention Time and SIM Ions for 11 Organic Tin Compounds and Internal Standards

No.	Compound	RT (min)	Quantifier ion	Qualifier ion (s)		
I.S.	Tributyl tin-D27	8.529	217	281	318	
1	Dimethyl tin	3.450	179	177	151	135
2	Methyl tin	4.358	193	165	191	163
3	Di-*n*-propyl tin	6.492	235	193	233	191
4	Butyl tin	6.557	235	177	179	233
5	Di-butyl tin	7.691	263	207	205	261
6	Tri-butyl tin	8.643	291	289	205	207
I.S.	Tetra-butyl tin-D36	9.314	190	254	318	
7	*n*-Octyl tin	9.130	291	177	179	289
8	Tetra-butyl tin	9.452	291	177	179	235
9	Di-phenyl tin	10.853	301	275	195	305
I.S.	Tri-phenyl tin-D15	12.874	366	364		
10	Di-*n*-octyl tin	11.821	375	261	179	263
11	Tri-phenyl tin	12.910	351	349	347	197

Results and Discussion

Calibration solutions

A six-level 11-component organic tin compounds calibration curve was evaluated over the concentration range 1.0 to 200 µg/L. Figure 2 shows the SIM overlay total ion chromatogram of six levels. As indicated in Table 5, all of the organic tin compounds achieved excellent linearity, with a linear coefficient R^2 greater than 0.996.

Table 5. Calibration Results of Organic Tin Compounds

Compound	Range of linearity (µg/L)	Correlation coefficient (R^2)
Diethyl tin	1 ~ 282	0.9962
Methyl tin	1 ~ 200	0.9997
Di-*n*-propyl tin	2 ~ 279	0.9999
Butyl tin	2 ~ 259	0.9999
Di-butyl tin	2 ~ 236	0.9999
Tri-butyl tin	2 ~ 234	0.9999
n-Octyl tin	1 ~ 187	0.9999
Tetra-butyl tin	2 ~ 262	0.9998
Di-phenyl tin	1 ~ 206	0.9999
Di-*n*-octyl tin	1 ~ 159	0.9996
Tri-phenyl tin	1 ~ 198	0.9998

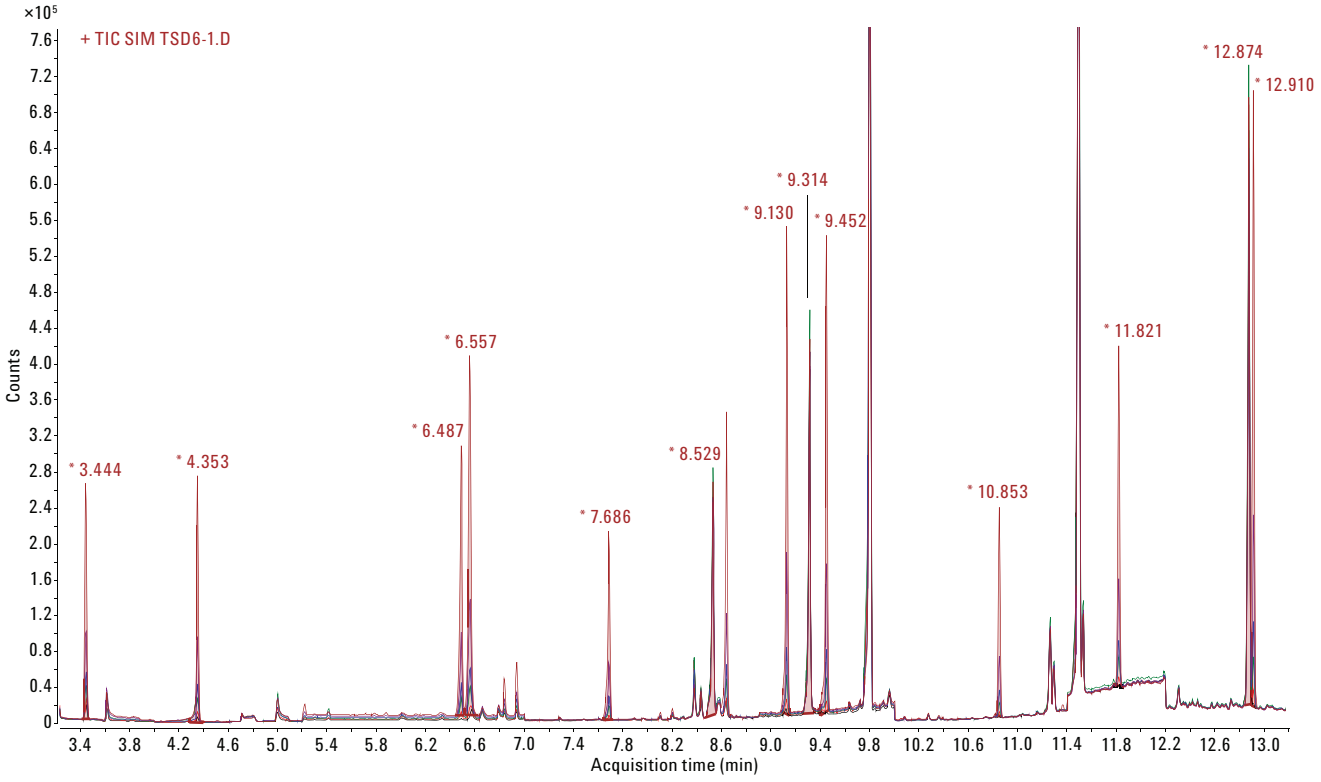

Figure 2. SIM Ions overlay chromatogram of six levels for organic tin compounds.

Each calibration level was injected seven times for evaluation. The RSD under six different calibration levels is shown in Table 6. Most of the RSD results were below 5 %, even at an extremely low concentration level of 1.5 µg/L, illustrating satisfactory reproducibility.

The instrument sensitivity is excellent. Figure 3 shows the SIM ion chromatogram of 11 organic tin compounds for the lowest calibration level (~ 1 µg/L).

Table 6. RSD% Result of Organic Tin Compounds for Six Calibration Levels (n = 7)

Compounds	Std 1 (~ 1.5 µg/L)	Std 2 (~ 6.0 µg/L)	Std 3 (~ 15 µg/L)	Std 4 (~ 30 µg/L)	Std 5 (~ 75 µg/L)	Std 6 (~ 225 µg/L)
Diethyl tin	7.29	4.39	3.00	0.68	0.54	0.68
Methyl tin	1.28	0.88	1.62	0.63	0.76	0.5
Di-*n*-propyl tin	4.44	1.26	1.73	0.53	1.01	1.04
Butyl tin	3.20	1.08	1.69	0.63	0.85	1.03
Di-butyl tin	2.49	0.85	1.98	0.57	1.01	0.98
Tri-butyl tin	4.49	1.68	1.88	0.44	1.28	1.21
n-Octyl tin	1.50	1.70	2.00	0.83	0.85	1.20
Tetra-butyl tin	6.94	1.85	1.80	0.71	1.17	0.94
Di-phenyl tin	4.08	1.16	2.08	0.46	0.87	0.85
Di-*n*-octyl tin	3.10	1.15	2.20	0.83	1.27	1.55
Tri-phenyl tin	4.58	1.04	2.24	0.67	0.94	1.17

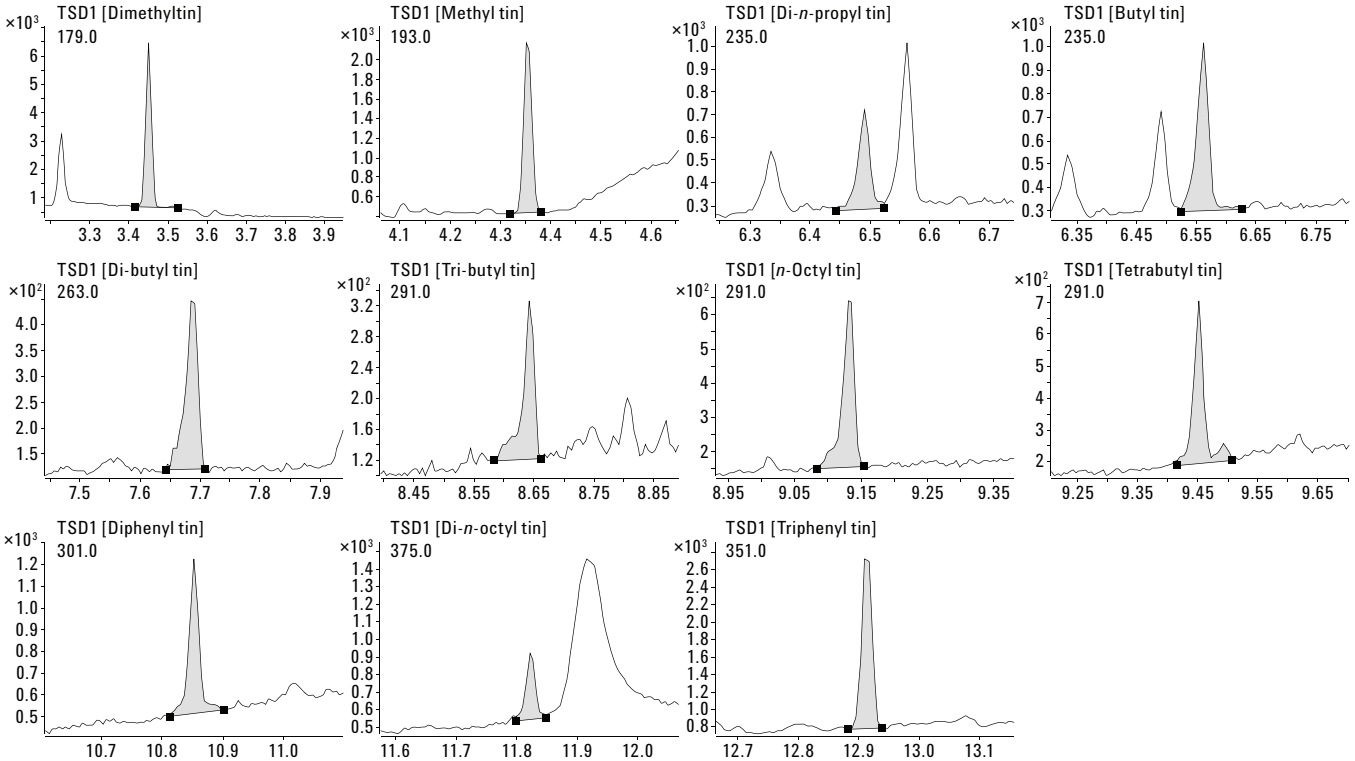

Figure 3. SIM ion chromatogram of 11 organic tin compounds for the lowest calibration level.

Instrument detection limits (SNR > 3) of each organic tin compound is calculated by signal-to-noise ratio (S/N) of lowest concentration (Table 7). For all the organic tin compounds, the instrument detection limits are below 1.0 µg/L, which meets the EN 71-3 regulation requirement.

Table 7. S/N at the Lowest Calibration Level and Instrument Detection Limit

Compound	Lowest concentration (µg/L)	S/N (peak-to-peak)	Instrument detection limit (µg/L)
Diethyl tin	1.88	19	0.30
Methyl tin	1.33	91	0.04
Di-*n*-propyl tin	1.86	29	0.19
Butyl tin	1.73	40	0.13
Di-butyl tin	1.57	27	0.17
Tri-butyl tin	1.56	6	0.78
n-Octyl tin	1.25	30	0.13
Tetra-butyl tin	1.75	19	0.28
Di-phenyl tin	1.38	16	0.26
Di-*n*-octyl tin	1.06	12	0.27
Tri-phenyl tin	1.32	29	0.13

Toy material sample analysis: Spike recovery and reproducibility

Three types of toy materials, representing three categories of EN71-3 were analyzed. Each category had two different toy samples (Figure 4): Category I: crayon (Sample A) and plasticene (Sample B) , Category II: bubble solution (Sample A) and paint (Sample B), Category III: soft plastic (Sample A) and cloth (Sample B). All of the samples were prepared by the migration and dervatization procedure described above and then analyzed by GC/MS.

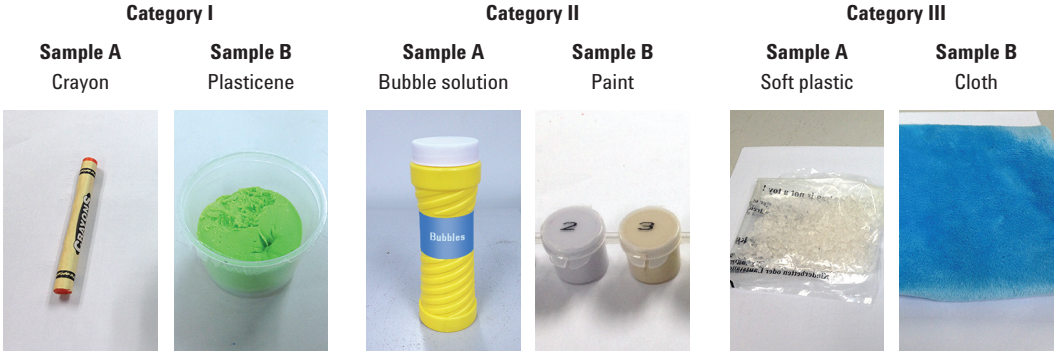

Figure 4. Six toy materials for recovery test represent three categories into EN71-3.

The spike recovery test of organic tin compound was using the migration solutions. Category I and Category III toy samples were spiked at two concentration levels of 20 µg/L and 40 µg/L. Category II samples were spiked at three concentration levels of 4 µg/L, 20 µg/L, and 40 µg/L. The lowest migration solution spike level of 4 µg/L for Category II and 20 µg/L for Categories I and III just meet the migration limits from toy material in EN 71-3 (0.2 mg/kg for Category II, 0.9 mg/kg for Category I). The method evaluated six parallel spike samples for each level. The result of the spike recovery and reproducibility is shown in Table 8.

As indicated in these tables, with the exception of paint and plasticene which contain trace amounts of methyl tin and dimethyl tin, good recoveries were obtained for all the other investigated organic tin compounds, ranging from 80 to 120 %, and relative standard deviation (RSD) less than 10 % for more than 96 % of the parallel spike samples. All of the results demonstrated the excellent recovery and reproducibility of the method, especially at limit concentration level.

Table 8A. Recovery Data for Category I Toy Material Spiked with Organotins

Category I	**Sample A: Crayon**				**Sample B: Plasticene**			
	20 µg/L		**40 µg/L**		**20 µg/L**		**40 µg/L**	
Compound	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**
Diethyl tin	106	2.09	106	2.20	130	2.21	128	2.62
Methyl tin	122	4.57	110	7.22	171	13.2	152	4.10
Di-*n*-propyl tin	110	1.59	105	1.44	105	0.91	103	0.84
Butyl tin	123	2.26	112	7.2	128	9.61	118	3.00
Di-butyl tin	110	1.63	105	1.38	108	1.37	104	1.39
Tri-butyl tin	109	1.00	104	1.43	108	1.51	104	0.64
n-Octyl tin	111	1.49	106	3.71	90	4.96	84	1.98
Tetra-butyl tin	106	2.16	106	5.99	98	3.23	90	1.53
Di-phenyl tin	106	0.40	105	0.94	110	1.73	107	0.47
Di-*n*-octyl tin	110	1.70	109	2.41	104	2.75	103	1.66
Tri-phenyl tin	107	0.52	103	0.69	108	2.1	104	0.73

Table 8B. Recovery Data for Category II Toy Material Spiked with Organotins

Category II	**Sample A: Bubble solution**						**Sample B: Paint**					
	4 µg/L		**20 µg/L**		**40 µg/L**		**4 µg/L**		**20 µg/L**		**40 µg/L**	
Compound	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**	**Recovery %**	**RSD %**
Diethyl tin	96	5.43	106	3.68	111	3.71	155	3.25	154	2.22	145	6.57
Methyl tin	88	13.6	79	10.3	115	8.62	122	5.37	135	4.33	102	13.39
Di-*n*-propyl tin	76	7.01	85	2.32	90	3.21	79	1.78	79	2.72	80	5.23
Butyl tin	73	9.37	73	5.24	95	3.80	80	3.63	82	4.22	69	6.76
Di-butyl tin	84	5.81	93	1.36	94	2.21	90	1.55	87	0.73	87	3.89
Tri-butyl tin	82	4.77	92	1.42	95	1.60	100	1.22	97	0.96	95	1.54
n-Octyl tin	93	4.46	95	1.12	99	1.77	87	3.47	83	1.56	73	2.18
Tetra-butyl tin	99	3.43	94	5.42	100	1.70	117	11.7	108	8.17	123	36.6
Di-phenyl tin	102	3.19	102	1.27	105	1.51	116	3.31	113	2.33	106	3.67
Di-*n*-octyl tin	72	3.44	82	3.35	82	3.14	113	5.11	116	6.38	110	2.34
Tri-phenyl tin	88	4.87	93	1.00	96	1.59	98	1.35	95	0.89	93	1.10

Table 8C. Recovery Data for Category III Toy Material Spiked with Organotins

Category III	Sample A: Soft plastic				Sample B: Cloth			
	20 µg/L		40 µg/L		20 µg/L		40 µg/L	
Compound	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %	Recovery %	RSD %
Diethyl tin	96	2.42	94	2.24	113	1.81	105	1.48
Methyl tin	125	5.30	109	2.89	130	2.94	111	2.33
Di-*n*-propyl tin	97	1.78	94	2.52	97	2.11	94	1.36
Butyl tin	115	3.84	105	2.56	106	2.31	97	2.21
Di-butyl tin	97	1.40	96	3.87	97	2.14	95	1.48
Tri-butyl tin	97	0.67	96	1.35	97	1.74	95	1.60
n-Octyl tin	98	3.77	97	2.62	93	1.05	88	1.86
Tetra-butyl tin	90	9.46	94	6.06	91	3.43	90	6.72
Di-phenyl tin	96	4.43	97	4.08	104	2.95	95	1.23
Di-*n*-octyl tin	94	7.23	103	10.5	97	6.35	88	1.64
Tri-phenyl tin	95	1.74	96	1.09	95	1.52	95	1.55

Conclusion

The use of the Extractor EI source in an Agilent 5977A Series GC/MSD can provide excellent sensitivity and stability for the analysis of organotin compounds in toy materials. Instrument detection limits were lower than 1 µg/L for all the compounds. Calibration from 1.0 to 200 µg/L showed excellent linearity, as measured by coefficient $R^2 > 0.996$. Moreover, good recovery and reproducibility were also achieved for the analysis of organotin compounds in three categories toy materials. As a result, the 5977A Series GC/MSD was demonstrated to meet the requirements of EN 71-3: 2013 for the determination of organic tin compounds in toys.

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