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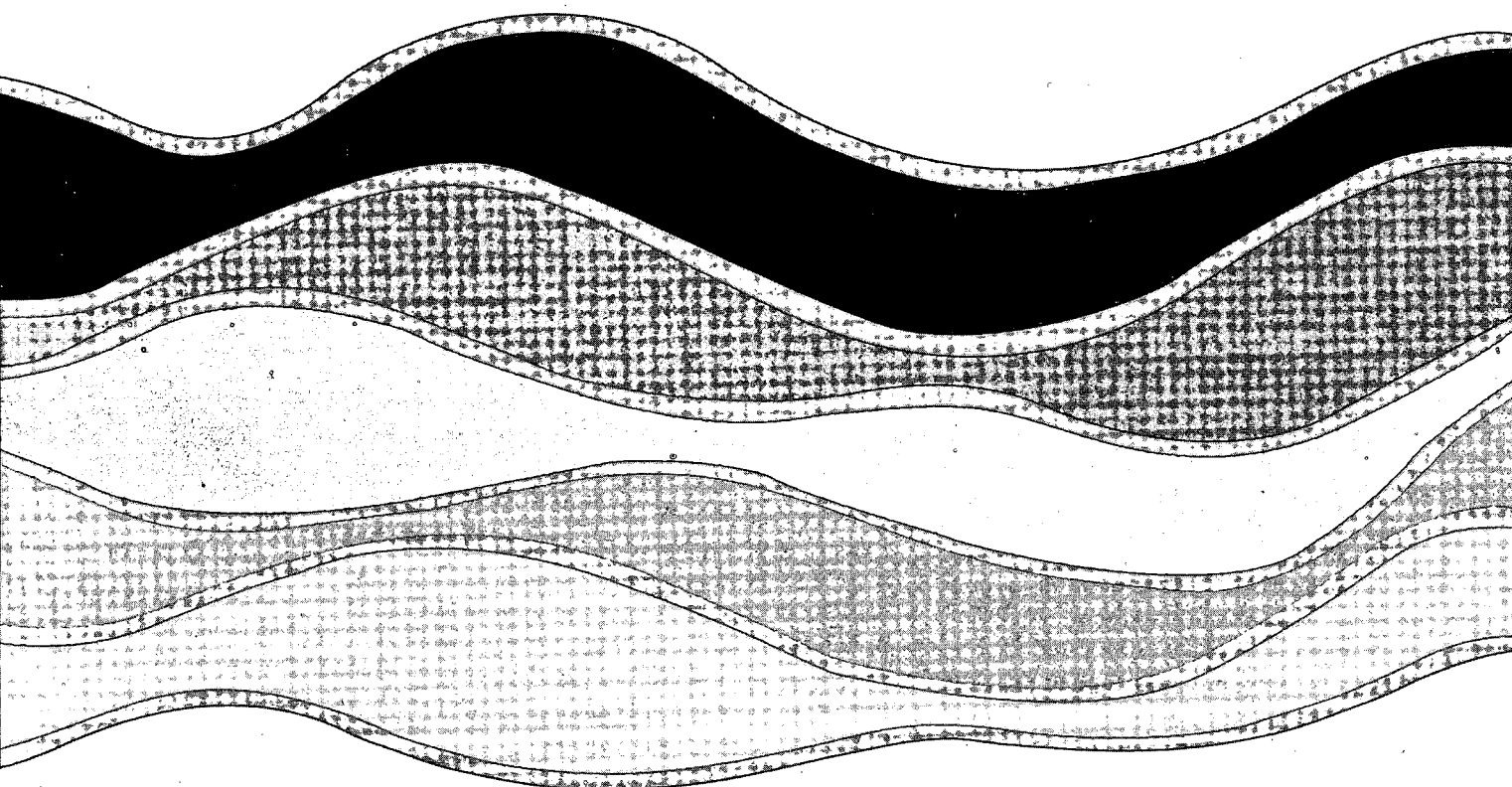
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**DETERMINATION OF BUTYLtin SPECIES IN SEWAGE AND
SLUDGE**

Y.K. Chau, S. Zhang & R.J. Maguire

NWRI CONTRIBUTION 91-64

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DETERMINATION OF BUTYLTIN SPECIES IN
SEWAGE AND SLUDGE

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NWRI Contribution 91-64

Management Perspective

A method for the extraction and determination of butyltin species in sewage materials has been developed in conjunction with a survey of the occurrence of butyltin compounds in several Canadian sewage treatment plants. In this method, the various butyltin and the acid-leachable Sn(IV) species are quantitatively extracted by tropolone in toluene, followed by ethylation to their tetraalkyl-substituted forms, all of which can be determined by a GC-AAS technique. The non-pesticidal octyltin species can also be determined by this method. Analyses of some samples from several Canadian sewage treatment plants are given.

The overall objectives of this program of research are (i) to assess tributyltin occurrence in sewage treatment plant influents and effluents as a result of uses other than antifouling uses, and (ii) to assess the occurrence of non-pesticidal organotins in sewage treatment plant influents and effluents. The former objective contributes to DOE's pesticide responsibilities, while the latter objective is work identified in the CEPA assessment of non-pesticidal organotins. This study was supported in part by PESTFUND and CEPA funding.

PERSPECTIVES DE LA DIRECTION

Une méthode d'extraction et de dosage des espèces de butylétain dans des eaux usées a été mise au point de concert avec une étude sur la présence de composés de butylétain dans plusieurs stations canadiennes d'épuration des eaux usées. Cette méthode permet d'effectuer une extraction quantitative au tropolone dans le toluène des différentes espèces de butylétain et espèces d'étain (IV) qui peuvent être libérées par lixiviation acide, suivie d'une éthylation à leurs formes tétraalkylées, qui toutes peuvent être dosées par chromatographie en phase gazeuse et spectrométrie par absorption atomique. Cette méthode peut aussi servir à doser l'espèce d'octylétain autre qu'un pesticide. Les résultats d'analyse de quelques échantillons provenant de plusieurs stations d'épuration des eaux usées au Canada sont indiquées.

Les objectifs généraux de ce programme de recherche sont i) l'évaluation de la présence du tributylétain dans les affluents et les effluents de stations d'épuration des eaux usées découlant d'usages autres que peinture antisouillure et ii) l'évaluation de la présence de produits organostanniques autres que des pesticides dans les affluents et les effluents de stations d'épuration des eaux usées. Le premier objectif permet au ministère de l'Environnement d'assumer ses responsabilités dans le domaine des pesticides, tandis que le dernier correspond à des travaux effectués dans le cadre de l'évaluation des composés organostanniques autre que des pesticides en vertu de la LCPE. La présente étude a été financée en partie par PESTFUND et la LCPE.

ABSTRACT

A method for the extraction and determination of butyltin compounds in sewage and sludge is reported. Sewage and sludge samples are acidified and shaken for 2 hr. The various butyltin and the acid-leachable Sn(IV) species are quantitatively extracted by tropolone in toluene, followed by ethylation to their tetraalkyl-substituted forms, BuSnEt_3 , Bu_2SnEt_2 , Bu_3SnEt and Et_4Sn , all of which can be determined by a GC/AAS technique. The non-pesticidal octyltin species can also be determined by this method. Detection limits expressed as Sn are 40 ng/L and 2 ng/g dry wt. for sewage and sludge respectively. Analyses of some samples from Canadian treatment plants are given.

RÉSUMÉ

On décrit une méthode d'extraction et de dosage des composés de butylétain dans les eaux usées et les boues. Des échantillons d'eaux usées et de boues sont acidifiés et agités pendant 2 heures. On procède à l'extraction quantitative au tropolone dans le toluène des différentes espèces de butylétain et espèces d'étain (IV) qui peuvent être libérées par lixiviation acide, suivie d'une éthylation à leurs formes tétraalkylées, BuSnEt_3 , Bu_2SnEt_2 , Bu_3SnEt et Et_4Sn , qui toutes peuvent être dosées par chromatographie en phase gazeuse et spectrométrie par absorption atomique. Cette méthode peut aussi être utilisée pour doser l'octylétain autre qu'une pesticide. Les limites de détection exprimées sous forme de Sn sont respectivement de 40 ng/L et de 2 ng/L de poids sec pour les eaux usées et les boues. Les résultats d'analyses de certains échantillons sont indiqués.

Determination of Butyltin Species in Sewage and Sludge

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Butyltin compounds have been found in various types of environmental samples. Recently, a study has been carried out to examine the occurrence of butyltin residues in sewage treatment plants before and after treatment in order to assess their treatability in the treatment plants. Sewage samples consist of extremely complex and unknown matrices, which require special treatment before analysis. Analytical procedures designed for speciation usually are not compatible with rigorous digestion. Very limited information on the analysis of sewage materials is available¹. There is basically no information on the sample treatment of sludge materials. The present study reports on the evaluation of several digestion/extraction techniques with the aim of developing an analytical procedure for the speciation of the different butyltin compounds in the influent, effluent, and sludge samples of municipal sewage treatment plants. These methods are being used in a survey of the occurrence of butyltin compounds in several major municipal treatment plants in Canada. Results of the survey will be published elsewhere.

Experimental

Materials and Methods

Monobutyltin chloride, dibutyltin dichloride and tributyltin chloride were obtained from Alfa

Products, Ward Hill, MA. Tropolone and ethylmagnesium bromide (2.0M in tetrahydrofuran) were supplied by Aldrich, Milwaukee, WI. Standard butyltin solutions (1000 $\mu\text{g/mL}$ as Sn) were prepared by dissolving appropriate amounts of the butyltin compounds in water. The internal standard addition technique was used in the calculation of the concentrations of butyltin.

The butyltin species were determined by a gas chromatography-atomic absorption spectrometry method². The butyltin and Sn(IV) species were extracted in tropolone followed by ethyl derivatization to the tetra-alkyl substituted forms for the GC-AAS determination. Di-octyltin species can also be determined by this technique. A chromatogram showing the various Sn species is shown in Figure 1.

Sewage samples used for the investigation were obtained from the Toronto Humber and Greater Vancouver Sewage Treatment Plants. Samples were stored in a cold room at 5°C in brown bottles until use. For assessment of extraction recoveries, sewage and sludge samples were spiked with 2.0 μg of each of the butyltin standards and equilibrated by shaking for 2 hr before they were analyzed.

Digestion of sludge samples by room temperature acid treatment

Samples (150 mL) of a well mixed sludge after spiking with known amounts of each of the butyltin species were first subject to acid treatment by adding *ca.* 10 mL of conc. hydrochloric acid in a 250 mL separatory funnel and allowed to stand inside a fume cupboard for 1-2 hr until the gas evolution subsided. After adjustment of the pH of the solution to 1-2, the samples were shaken in a mechanical shaker for 2 hr. followed by extraction with 20 ml of 0.5% tropolone in toluene for 4 hr with addition of 60 g NaCl. An aliquot (5 mL) of the extract was removed

and evaporated to almost dryness on a heating block at 30°C with the aid of a nitrogen stream. The volume was adjusted to 1 mL with hexane and allowed to react with 0.2 mL of ethylmagnesium bromide (2.0M in tetrahydrofuran) for 10 min. The excess of ethylmagnesium bromide was destroyed by shaking with 2 mL of 0.5M sulfuric acid. The hexane phase containing the derivatized butyltins and Sn(IV) was subjected to a clean up procedure by loading 0.5 mL of the hexane extract into a glass column (15 cm H x 1.5 cm dia.) containing *ca.* 6 g of silica gel (containing 5% water), packed from bottom to top in the following order: glass wool, 1 cm anhy. Na₂SO₄, silica gel bed, 1 cm Na₂SO₄. The butyltin compounds were eluted with 30 mL of hexane at the rate of 0.5 mL/min. After reduction of the eluent volume to 0.5 mL in a rotary evaporator, a suitable aliquot was injected into the GC-AAS system for the analysis of the butyltin and Sn(IV) species. The results were expressed as µg Sn per g of sludge on dry weight basis. The dry weight of sludge was obtained by drying several well-mixed aliquots of sludge samples at 30°C to obtain their averaged dry weight.

Digestion of sludge samples by acid reflux

After acid treatment, samples (150 mL) of sludge were placed in 500 mL round bottomed flasks and refluxed at *ca.* 60°C for 2 hr. After cooling, the samples were extracted with 20 mL of 0.5% tropolone in toluene for 4 hr with addition of 60 g NaCl. The toluene extract was evaporated and made up to 1 mL with hexane for subsequent derivatization and clean up as mentioned above.

Extraction of butyltin species in sludge

The room temperature acid treated samples (150 mL) of sludge were extracted with 20 ml of

the following extractants for 4 hr in a mechanical shaker after addition of 60 g NaCl. After extraction the samples were processed in a similar manner as described in the previous paragraph to evaluate their extraction recoveries.

1. Toluene
2. Dichloromethane
3. 0.5% tropolone in hexane
4. 0.5% tropolone in dichloromethane
5. 0.5% tropolone in toluene
6. 0.5% tropolone in toluene after acid reflux for 2 hr

Extraction of butyltin species from sewage samples

Sewage samples (200 mL) were originally acidified to pH 1 with HCl at the time of collection. The pH was checked and the dissolved gases were allowed to evolve before the extraction. The sample was extracted with 20 mL of 0.5% tropolone in toluene for 4 hr after adding 60 g NaCl. The extract was processed and ethylated in the same manner as described above for sludge samples. The clean-up was carried out using a pasteur pipet as a column (15 cm L, 5 mm dia. containing *ca.* 1 g of silica gel (5% water), packed in a similar manner as for the regular column mentioned above, and eluted with 25 mL of 10% ethyl ether in hexane at a rate of 0.7 mL/min. After reduction of the eluent volume to 0.5 mL, the extract was analyzed in the GC-AAS system.

Results and Discussion

Sewage and sludge materials consist of complex and unknown matrices, and must be subject to proper digestion procedures in order to break down the organic materials to release the molecular and ionic butyltin compounds. In any direct speciation procedure, the digestion procedure must be carefully chosen so as to destroy the matrices but not to affect the authentic

forms of the analyte molecules.

Of all the extractants investigated for the extraction of butyltin compounds from the acid-treated sludge (Table I), toluene alone can recover the Bu_2Sn and Bu_3Sn species but not the BuSn or Sn(IV) species. Tropolone must be used as an extractant and toluene as solvent for quantitative recovery of BuSn and Sn(IV) . It is imperative that the sludge samples be acidified prior to extraction for two reasons: first to expel all gases from the sample, and secondly to release the analytes from the particulate matter. Similar phenomena were also observed in the extraction of butyltin compounds from sediment³. Room temperature acid treatment released the tin species as efficiently as the acid reflux technique. For the sake of convenience, room temperature acid treatment was recommended as the procedure for sludge digestion. A second extraction with any of the extractants did not improve the recovery to any significant extent. In the acid-reflux sample treatment, more inorganic Sn(IV) was released than in the 2 hr room temperature acid treatment. The Sn(IV) species was still found in three consecutive extractions with tropolone in toluene, whereas no significant quantities of butyltin species was found in the second extraction. Therefore, the Sn(IV) values from the acid sample treatment technique can only be regarded as acid-leachable Sn(IV) . If accurate determinations of Sn(IV) is required, acid-reflux sample treatment must be used and repeated extractions up to three times should be performed, or alternatively, it may be determined as total Sn by atomic absorption methods after rigorous digestion.

The effect of extraction time was investigated by shaking the sludge samples with a 0.5% tropolone in toluene solution for 2 and 4 hr intervals. It was observed that 2 hr shaking only

recovered 54% of the monobutyltin species, while all the other butyltin species in sludge were recovered quantitatively after 4 hr shaking. For thorough extraction, a 4 hr period was also adopted for sewage samples.

Clean-up for sludge must be incorporated in the procedure. In this connection, silica gel (5% water) was found satisfactory. A larger capacity column was necessary for sludge, whereas a smaller, more convenient pasteur pipet could be used as column for sewage samples which contained relatively lesser amounts of organic matter. As sludge contains a more complex matrix, the volume of the eluent used must be investigated for a particular type of sludge. Hexane could be used to release all the butyltin and Sn(IV) species without co-eluting the organics. Under the present conditions, the 15 cm x 1.5 cm dia. column was sufficient to retain the organic matter in a brown colored band 2 cm wide at the top when 150 mL (ca. 4.5 g dry wt.) of sludge suspension was used and eluted with 35 mL of hexane. In a smaller column operation for sewage samples, there is less colored material and a light-brown color band was observed. The extraction procedure for sludge was readily applicable to sewage samples. In both cases, acidification of sample was necessary.

Recovery of Sn(IV) and butyltin species from sewage and sludge was investigated by spiking known amounts of the compounds into samples of relatively low butyltin content, and carrying out the analysis in replicates. It was observed that the recovery ranged from 89 to 114% at a spike level of 1 to 5 μg (Table II). The precision of the method was assessed by running replicate ($n=6$) analyses of spiked samples (2 μg of each of Sn(IV) and butyltin species) to 150 mL of sewage and 100 mL of sludge respectively. Coefficients of variation for sewage at this

level were 4, 6, 11 and 8% respectively for the Sn(IV) , BuSn^{3+} , $\text{Bu}_2\text{Sn}^{2+}$, and Bu_3Sn^+ species. Coefficients of variation for sludge samples spiked at the same level were 10, 8, 9, and 9% for Sn(IV) , BuSn^{3+} , $\text{Bu}_2\text{Sn}^{2+}$, and Bu_3Sn^+ respectively. Detection limits (as Sn) under the present operation conditions are 40 ng/L and 2 ng/g dry wt. for sewage and sludge respectively. Analyses of some samples from Canadian treatment plants are given in Table III to show the application of this method.

For sample preservation, it is recommended to add 2 mL of conc. HCl per litre of sewage sample immediately after collection to reduce the absorption of the analytes on container walls and to release the analytes from particulate matter in solution. Sample bottles for sewage and sludge should be placed in coolers with lids loosely capped during transportation especially in summer time. Plastic bottles and other plastic ware should not be used in sampling because of the use of dibutyltin and monobutyltin as poly(vinyl chloride) stabilizers. Sludge samples should be analyzed as soon as possible after collection to minimize biological action resulting in chemical species transformation. We have noticed that sewage samples after acidification can be stored for a period of up to one month in brown bottles in the dark at 5°C without changes in butyltin species distribution. Since sludge materials are highly bio-active, storage is not advisable unless the sample has been chemically processed. The stability of butyltin species in sludge samples was not investigated.

In summary, the method is applicable to the determination of butyltin species in sewage and sludge materials. The acid treatment is efficient for release of the butyltin compounds quantitatively from the complex sewage matrices. The GC-AAS technique is specific and

sensitive for this purpose.

This study was supported in part by PESTFUND and a Canadian Environmental Protection Act fund (CEPA) of the Department of Environment.

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Table 1. Recovery of butyltin species from sludge by different extraction methods

Extractant/Solvent	Sn ⁴⁺	BuSn ³⁺	Bu ₂ Sn ²⁺	Bu ₃ Sn ⁺
Toluene	-	46	82	94
Dichloromethane	-	-	-	-
0.5% Tropo/hexane	-	-	76	49
0.5% Tropo/dichloromethane	-	-	103	113
0.5% Tropo/Toluene	96	90	114	107
0.5% Tropo/Toluene after acid reflux	88	68	95	95

Recovery is evaluated by spiking 2.0 μg of each of the butyltin and Sn(IV) species to 150 ml (ca. 3 g dry wt.) of sludge samples. After blank correction, the values are compared to extraction of the same amount of standards without the sludge. The recovery represents absolute recovery from sludge materials. Recovery is the average of two replicates. (-) no recovery.

Table 2. Recovery of butyltin compounds from spiked sewage and sludge samples

Sewage samples

Spike (μg)	Sn^{4+}	BuSn^{3+}	$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+
1	110	101	99	99
2	91	101	107	90
5	106	109	109	104

Sludge samples

Spike (μg)	Sn^{4+}	BuSn^{3+}	$\text{Bu}_2\text{Sn}^{2+}$	Bu_3Sn^+
1	84	103	95	95
2	105	100	89	114
5	91	96	94	91

Sewage (effluent) samples were from the Toronto Humber Sewage Treatment Plant with the following butyltin content: Sn(IV) , $5.2 \mu\text{g/l}$; no detectable butyltin species. Spikes were added to 200 ml of sewage samples, equilibrated by shaking for 2 hr before analysis. Results were average of independent duplicate analysis.

Sludge samples were from the Vancouver Sewage Treatment Plant with the following butyltin content: Sn(IV) , $5.9 \mu\text{g/g}$ dry wt.; no detectable butyltin species. Spikes were added to 100 ml (ca. 2.0 g dry wt.) of the well-shaken sludge suspension, equilibrated by shaking for 2 hr before analysis. Results are average of independent duplicate analysis.

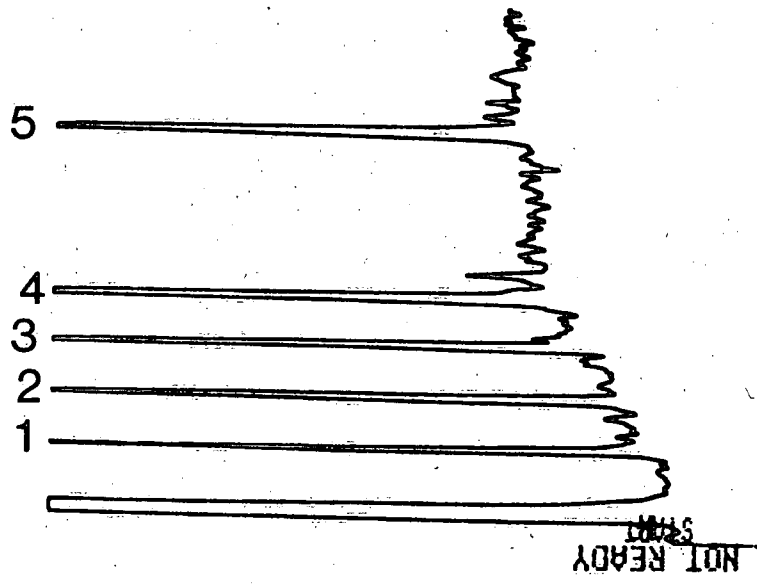
Table III. Analysis of butyltin and acid-leachable Sn(IV) species in sewage and sludge in some Canadian treatment plants.

Sewage	Sn ⁴⁺ (μg/L)		BuSn ³⁺ (μg/L)		Bu ₂ Sn ²⁺ (μg/L)		Bu ₃ Sn ⁺ (μg/L)	
	Infl.	Effl.	Inl.	Effl.	Infl.	Effl.	Infl.	Effl.
<u>Plant A</u>								
Sept. 90	-	-	10.7±0.7	8.7±0.1	2.4±0.1	2.0±0.3	-	-
Dec. 90	-	-	10.3±0.6	5.2±0.4	-	-	-	-
<u>Plant B</u>								
Sept. 90	-	-	3.4±0.3	3.3±0.3	-	-	-	-
Dec. 90	-	-	5.5±0.4	1.3±0.3	-	-	-	-
<u>Plant C</u>								
Sept. 90	-	-	13.7±0.9	6.9±0.1	-	-	-	-
Dec. 90	27.5±2.1	9.2±0.2	5.7±1.1	9.5±0.2	-	-	-	-

Sludge	Sn ⁴⁺ (μg/g)	BuSn ³⁺ (μg/Kg)	Bu ₂ Sn ²⁺ (μg/Kg)	Bu ₃ Sn ⁺ (μg/Kg)
<u>Plant A</u>				
Sept. 90	9.3±0.5	-	-	-
Dec. 90	24.0±0	440±30	210±35	277.5±23
<u>Plant B</u>				
Sept. 90	5.8±0.3	-	20.5±0.5	130.5±2
Dec. 90	3.2±0.4	16.4±0	35.0±0.5	45.5±3
<u>Plant C</u>				
Sept. 90	192.6±7.4	-	-	-
Dec. 90	40.7±0	-	-	-

Results are average of duplicate analysis; Sewage sample, 200 mL; Sludge samples, 150 mL suspension; results expressed on dry wt. basis. (-) not detected. Detection Limits (as Sn) for sewage, 40 ng/L; for Sludge, 2 ng/g dry wt.

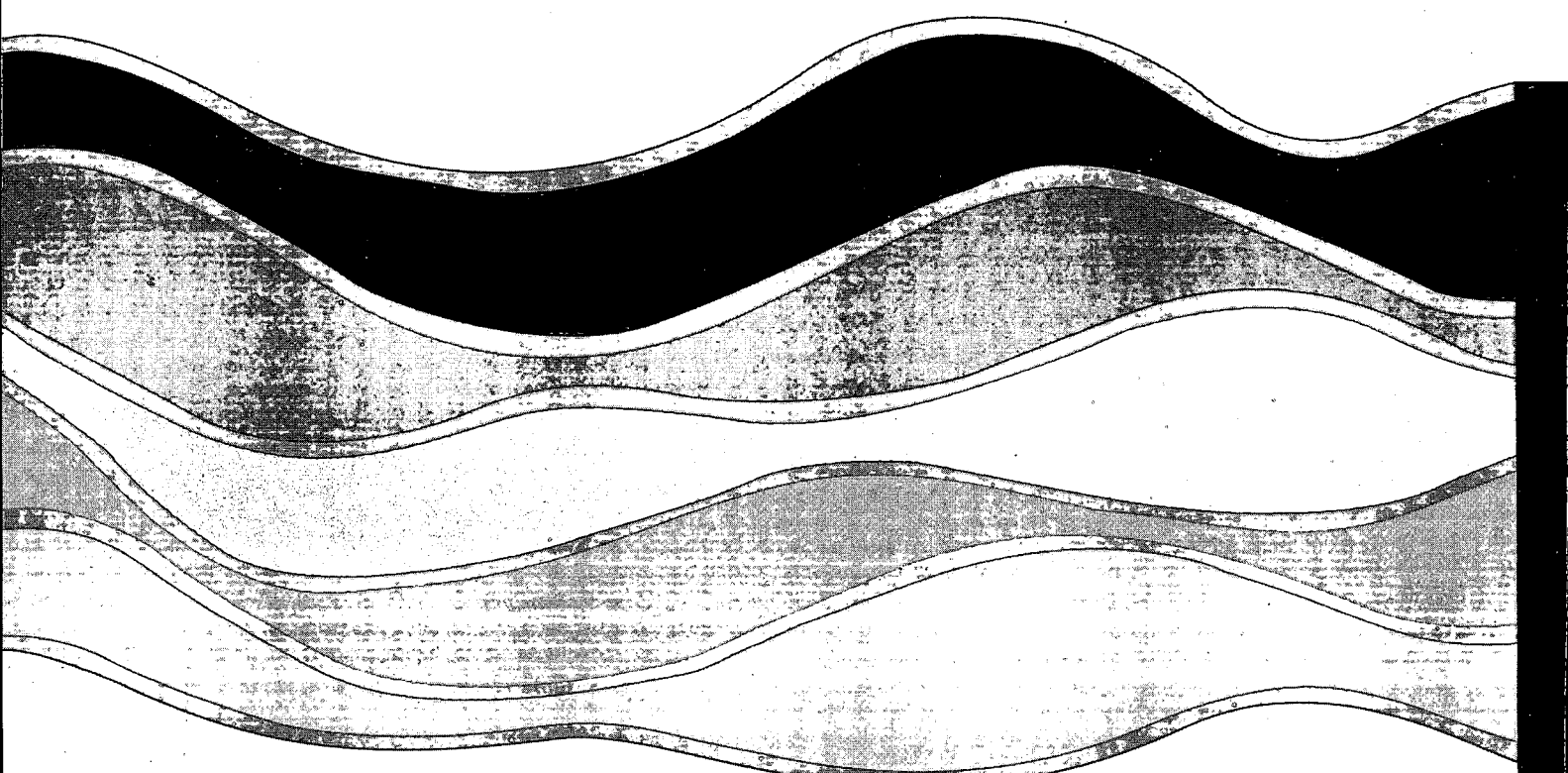
Fig. 1. Chromatogram showing 1- Sn(IV) , 2- BuSnEt_3 , 3- Bu_2SnEt_2 , 4- Bu_3SnEt and 5- $\text{Oct}_2\text{SnEt}_2$ species. Each peak represents ca. 2 ng as Sn.



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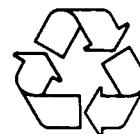


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