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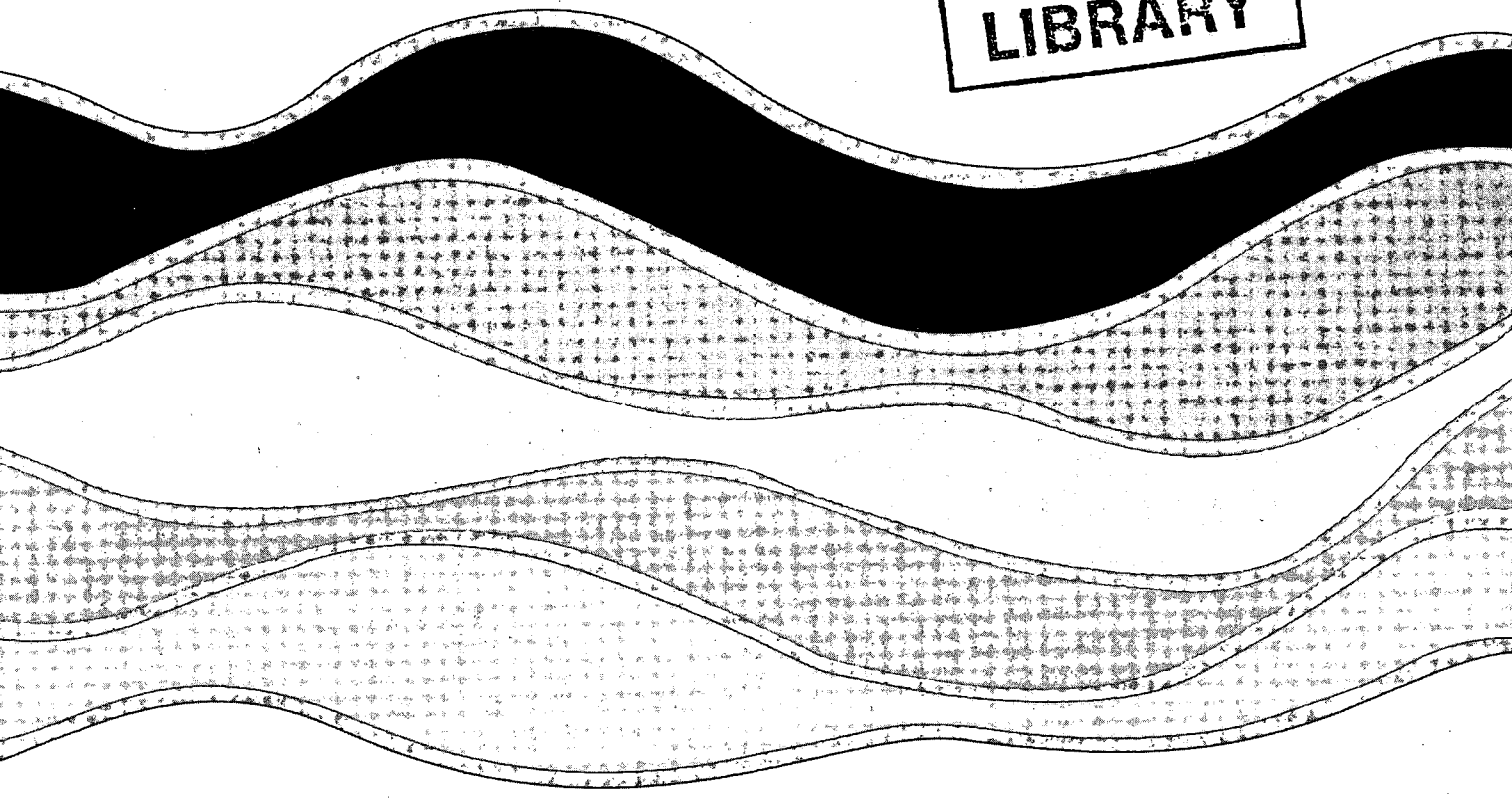

DETERMINATION OF BUTYLTIN SPECIES BY GC/ATOMIC EMISSION SPECTROSCOPY

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DETERMINATION OF BUTYLTIN SPECIES BY GC/ATOMIC EMISSION SPECTROSCOPY

by

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MANAGEMENT PERSPECTIVE

Using the atomic emission detector coupled to a gas chromatograph, a meth od was developed to speciate and quantify organotins. This method has an absolute detection limit of $7X10^{-12}$ g of tin which compares favourably with an ion spray MS/MS, which has a detection limit of $5X10^{-12}$ g but costs considerably more than an AED.

In addition, the emission spectra can be used to confirm the presence of Sn in the eluting peak. Environmental samples of fish and sediment were then analyzed for butyltins. Additional peaks related to tin compounds were observed in a number of sediment samples eluting about the time of the monobutyltin compound. Their identity is now being determined. The AED method is a quick and sensitive method to analyze for organotins at trace levels and the method can aid in determining the speciation of the compounds.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVE-GESTION

À l'aide d'un détecteur d'émission atomique couplé à un chromatographe à gaz, on a élaboré une méthode pour doser et distinguer les espèces des composés d'organoétain. Cette méthode a une limite de détection absolue de 7 $x10^{-12}$ g d'étain, qui se compare favorablement à celle d'un système SM/SM à pulvérisation ionique, qui a une limite de détection de $5x10^{-12}$ g, mais coûte beaucoup plus cher qu'un DEA.

En outre, le spectre d'émission peut également être utilisé pour consommer la présence de Sn dans le pic en élution. On a dosé les butylétains d'échantillons environnementaux de poissons et de sédiments. On a observé des pics supplémentaires en rapport avec des composés de l'étain dans un certain nombre d'échantillons de sédiments s'éluant à peu près en même temps que le monobutylétain, et on travaille à caractériser ces composés. La méthode du DEA est rapide et sensible pour l'analyse des organoétains à l'état de traces et cette méthode peut faciliter la caractérisation des espèces des composés.

M. J. Lawrence
Directeur
Direction de la recherche et des applications

ABSTRACT

A commercially available atomic emission detector coupled to a capillary column containing gas chromatograph was utilized to detect organotin compounds. The response for tin was found to be dependent on the flow rate of the make up gas. At flow rates of 174 mL/min, $6x10^{-12}$ g of tin could be detected. Lower flow rates decreased the sensitivity. Response curves for two different pressures were established and both plots exhibited curvature at low concentrations. Extracted fish and sediment samples were analyzed on the GC/AED system. The technique is element specific. The presence of tin compounds could be confirmed by examining the emission spectra taken at the retention time of the peak.

KEY WORDS: Atomic Emission Detector, Gas chromatograph, Organo tin, Speciation, Sediment, Fish.

RÉSUMÉ

On a utilisé un détecteur d'émission atomique du commerce couplé à un chromatographe à gaz à colonne capilaire pour détecter des composés de type organoétain. On a constaté que la réponse de l'étain dépendait du débit du gaz d'appoint. À des débits de 174 mL/min, on pouvait déceler la présence de 6×10^{-12}g d'étain. Des débits plus faibles diminuaient la sensibilité. On a tracé des courbes de réponse à deux pressions différentes et toutes deux présentaient une certaine courbure aux faibles concentrations. On a analysé des échantillons de poissons et de sédiments traités par extraction à l'aide du système GC/DEA. Cette technique donne des résultats spécifiques pour chaque élément. La présence de composés d'étain peut être confirmée par examen des spectres d'émissions obtenus pendant le temps de rétention du pic.

MOTS CLÉS : Détecteur d'émission atomique, chromatographe à gaz, organoétain, spéciation, sédiment, poisson.

INTRODUCTION

Organotins are mainly used as anti-fouling and stabilizing agents by industry and as pesticides in agriculture. Surveys[1] have shown that with the widespread use of tin, there is a concurrent widespread contamination by organotin of the aquatic environment. Indeed, organotins have been found in sediments[1], accumulated in the food chain by smaller organisms[2,3,4] and in fish tissue, both marine[5] and freshwater[1] species. In addition to these studies are the investigations of possible oxidation of tin by bacterial action[6] and other possible transformations of tin compounds in the environment[7]. In all these investigations, species differentiation and determination of the organotin compounds at environmental concentration levels are required. Analysis of these types is certainly one of the most challenging areas of research in analytical chemistry today.

The most effective and sensitive techniques for speciation of trace organometallic compounds are the tandem analytical systems consisting of an element-specific detector coupled to a chromatographic separation instrument. Atomic spectrophotometers, in the absorption and emission modes have been successfully used as detectors. Gas chromatography as well as liquid chromatography have been widely applied in the separation of organometallic compounds. Reviews on these methods are available[8,9,10].

For tandem analytical systems using gas chromatographic separations, derivatization is necessary to convert the polar and high boiling ionic organometallic species, such as R_3Sn^+, R_2Sn^{2+}, and RSn^{3+}, to volatile derivatives amenable to gas chromatographic separation. The most commonly used methods of derivatization are hydridization[11] or alkylation[12,13] using appropriate Grignard reagents. The derivatized extract containing tin is then injected onto a gas chromatograph equipped with a capillary or megabore column, the compounds separated and analyzed at a detector. A number of different

detectors have been used for this purpose. Various modes of atomic spectrometry have been utilized for specific metal detection after gas chromatographic separation, including atomic absorption[eg 12], plasma-excited atomic emission[14] and flame photometric detectors in the sulphur mode eg [15]. The other detector used is quadropole MS, in either the CI mode[16] or SIM mode[17]. The minimal detectable amount varies dependent on the detector, this value ranging from 0.01 ng[16] to 5 pg[18] depending on the detection system. Also these values are dependent on the compounds used[18], and whether the cited value is an experimentally measured value[18] or extrapolated[17].

It is this last aspect of detectors which is the focus of this report. Generally, the lower the detection limit, the more expensive the detection system. A detection limit similar to the lowest reported value for tin[18] (5pg) was achieved using a moderately priced, commercially available atomic emission detector. In addition confirmation of the presence of tin in the eluting peak of the chromatogram can be obtained from the emission spectra at the retention time of the peak down to levels of the minimum detectable concentrations. The minimum detectable amounts for the compounds used as standards was $6X10^{-12}$ g of the metal monitored at the detector. To successfully analyze for tin at these amounts, the operating conditions of the detector had to be altered from the manufacturers present recommendations. It is the optimizing of the operating conditions which will be reported as will typical results from standards, and sediment and fish samples. Ethylbutyltin compounds were used as standards.

METHODS

Each of the ethylbutyltins were prepared individually by dissolving the appropriate butyltin chloride precursor in distilled water, extracting with a tropolone-hexane(0.5%) at pH 1.5, then alkylating the extract with ethylmagnesium bromide[19]. Aliquots of triethylbutyl-, diethyldibutyl-, and ethyltributyltin were combined to provide an injection standard of 0.2 ng/uL of

each compound in spectrograde hexane. This standard was injected at increasing makeup gas flows. In another part of the study, the injection standard was diluted by a factor of two after duplicate injections. This solution was sequentially continually diluted by a factor of two until no response was observed on the chromatogram. Fish and sediment samples were extracted and prepared using procedures described elsewhere[20]. These samples were stored in a dark place at 4°C until needed for analysis. Duplicate injections were made of each sample as well as for each set of conditions where a standard was used.

The gas chromatograph was a Hewlett-Packard model 5890 equipped with a split/splitless injector for capillary columns. A pressure of 115 kPa was maintained at the column head. Helium carrier gas had a flow rate of 5 mL/min at an oven temperature of 90°C. The oven was programmed to have an initial temperature of 90°C which was increased to 200°C at a rate of 20°C/min and kept at this temperature for 5 min before cooling for the next determination. It was determined that there was no evidence of thermal decomposition of the standards in the injector at 250°C which was the temperature used for the study. All injections were performed in the splitless mode with the purge delay set at 0.8 min. The injection volume was 1 uL for all samples. An automatic sampler (Hewlett-Packard model 7321A) was used for all injections.

The detector was a Hewlett-Packard model 5921A atomic emission detector, which uses an induced microwave He plasma to excite the various atoms[21]. This was coupled to the gas chromatograph by a transfer line through which the end of the capillary column was directed to the plasma. The line was kept at a constant temperature of 210°C. For the initial studies, responses of the spectral lines of $Sn_{303.4nm}$, C_{496nm}, and H_{486nm} were used to prepare the chromatograms. For most of the study, only the $Sn_{303.4nm}$ line was needed. To obtain maximum emission for this line, the reagent gases of H_2 and O_2 were utilized. As the C_{496} and H_{486} emission lines require only O_2 as reagent gas, two separate injections on the same sample were needed when the three elements were analyzed. With hexane as the solvent, the solvent vent valve was activated at 1.5 min and shut off at 3.0 min to avoid extinction of the plasma. The detector cavity temperature was set at 210°C, and the plasma burned at a temperature of greater

than 3000°C. Results were transferred to a HP GC/AED/Data System work station to facilitate analysis. Occasionally between runs, O_2 was turned on for about a minute to burn off any Sn and C residues that might have collected at the end of the discharge tube. Make up gas flow rates were measured at the cavity vent outlet. Figures showing the emission spectra are presented with background noise subtracted from the spectra[22].

Columns, supplied by Hiresco (Mississauga, Ont), were 25m in length and had an internal diameter of 0.255 mm. The liquid phase was XE-52XL (5% phenyl methylpolysiloxane) with a film thickness of 0.25u. Flow rates were measured using a Humonics Optiflow 520 digital flowmeter (Fairfield, Ca) which permits an objective measure of the flows at higher values. Makeup gas flow rates were measured at the cavity vent outlet with the reagent gases and the spectrophotometer window purge gas turned off.

RESULTS AND DISCUSSION

The AE detector was previously used for analysis of heteroatom containing hydrocarbons. For these analyses the make up gas flow rate is optimized at 60 mL/min. Analysis for metals requires a higher flow rate, generally at 140 mL/min. To check the reproducibility of the system ten injections of the standard were made, 6 with a make up flow rate of 175 mL/min and four at 167 mL/min. At 175 mL/min, the triethyl- butyl-, diethyldibutyl-, and the ethyltributyltin mean responses were 999, 1587 and 1274 area counts respectively with corresponding relative standard deviations of 1.5%, 3.0% and 7.2%. Lowering the make up flow to 166 mL/min resulted in mean area responses of 759, 1118 and 958 respectively with corresponding relative standard deviations of 5.0%, 2.2% and 13.0%.

To establish the effect the make up gas flow rate has on the signal, duplicate injections of a 0.25x10-9g/uL standard solution containing the three butyltin compounds were made with increasing flow rate. The results of this are

illustrated in Fig. 1. Below a flow rate of 100 mL/min no signal was detected for all three tin compounds. A practical upper limit of 180 mL/min was adopted as higher flow rates could result in damage to the ferrules about the discharge tube which directs the column effluent into the plasma area. The curve in Fig. 1 exhibits a slow increase at low flow rates and increases rapidly above flow rates of 120 mL/min. The responses for all three tin compounds were still increasing at the 180 mL/min upper limit. A flow rate of 175 mL was used when analyzing samples and the flow rate was constantly monitored with no variation in the flow rate being observed. Other elements such as C, S, and N were normally monitored at make up flow rates of 60 mL/min. Increasing the flow rate diminished the response for these elements and they could not be monitored at the make up gas flow rates used to measure the various tin compounds. Therefore, no effort was made to check the response of the organic portion of the molecule during the tin analysis. Increasing the flow rate of the make up gas also increased the retention times of the peaks. Over the range of flow rates examined, the increase was 0.1 min.

Two calibration-type plots are shown in Fig. 2. One illustrates the responses for a flow rate of 171 mL/min and a maximum concentration of each tin species of 0.2×10^{-9} g injected. The other represents the responses for a flow rate of 160 mL/min and a maximum concentration of 1×10^{-9} g of each compound injected. At both flow rates, the points in the two plots are not linear over the concentration ranges studied, especially below concentrations of 10^{-10} g. As expected the lower detection limits for the three ethylbutyltin compounds are greater for those measured at the 160 mL/min flow rate of the make up gas than those measured at 171 mL/min. Also the responses for the three tin compounds, shown in Fig. 2, do not coincide when measured under the same conditions.

A typical chromatogram of the three tin compounds at concentrations of 0.2 ng/mL each is shown in Fig. 3. The three peaks have retention times of 4.99 min (Et_3BuSn), 6.17 min (Et_2Bu_2Sn), and 7.42 min ($EtBu_3Sn$). When the emission spectra is examined at one of these retention times, a plot similar to that in Fig. 4 is obtained. The peaks at 300.9 and 303.4 nm confirm that the compound examined does contain tin. The very minor peaks at 6.63, 7.69 and 8.49 min in

Fig. 3 were examined and their emission spectra exhibited the two characteristic tin peaks, indicating that these peaks were tin containing impurities in the standard solution.

As the response was not identical for the three butyltin compounds in the standard solution, it was necessary to ascertain if the difference in the response originated in the injection. This was done by comparing the results of a split injection (50:1 split ratio) of a standard butyltin solution (10^{-9}g/uL) to those from a splitless injection of the same solution. This was done in duplicate. The average area responses were 3365±10, 3325±10 and 3688±26 for Et_3BuSn, Et_2Bu_2Sn, and $EtBu_3Sn$ respectively in the splitless mode. The peak area responses of 59±5.2, 78±0.1 and 129±5.3 were measured using the split mode for the sample compounds. This indicated that there were more serious problems with the material being eluted in the split mode than in the splitless. Also the minimal detectable amounts are a function of the system including the injector and detector.

A number of sediment and fish samples were analyzed and the results are shown in Tables 1 and 2. As the recovery for the butyltins using this method is greater than 85%, no correction factor was applied to these concentrations. With the exception of sample F10, all of the fish samples listed in Table 1 contained measurable amounts of the three butyltin compounds. The measured quantities of tin compounds ranged from $5x10^{-12}$ to $149x10^{-12}$g. Generally, for each sample, the concentration of the tributyltin was greater than the dibutyltin which was greater than the monobutyltin. A typical chromatogram is shown in Fig 5 for fish sample F7. Only the three butyltin peaks are present with no other organo tin compounds being detected. At lower concentrations, such as in sample F6, the monobutyltin peak is less than four times the background noise. In this instance the presence of the tin compound was confirmed by inspection of the emission spectra[22].

The results for the sediment samples are listed in Table 2. Butyltin compounds were detected in all samples but with two samples containing only small amounts of the tributyltin compounds. Monobutyltin was detected in four of

the eleven samples at low concentrations. The AED chromatogram for sample S2 is shown in Fig.6. This chromatogram contains five integrated peaks, three of which are the ethylbutyltins and the two unidentified peaks which elute shortly after the triethylbutyltin at 5.20 and 5.29 min. As in the case of the chromatogram from the fish extract (Fig. 5), this chromatogram contains no interferences from other compounds extracted from the matrix, illustrating the selectivity of the AE detector. To ensure the two unidentified peaks represented tin containing compounds, the emission spectra were checked. The emission spectra for the 5.29 min. peak of sample S9 is shown in Fig. 7. This particular sample was chosen to be illustrated here as the concentrations of the components in the system are low with the peaks heights being closest to the value of twice the background level. The emission spectra shows to peaks at 303.4 and 300.9 nm, confirming the presence of tin. The emission spectrum for the peak at 5.21 min contains both tin emission lines, confirming that the other compound also contains tin. Values for the concentrations of these two compounds were estimated using the response curve for the monobutyltin. When detected both unknown compounds are present at about the same concentration and their concentrations are usually greater than that of monobutyltin.

CONCLUSION

In this study, the results derived from a new method to analyze organotin compounds has been reported. The AED method has a detection limit for tin comparable to lowest reported in the literature. By using a capillary column, the method allows the operator to discern between peaks representing different compounds which may not be resolved on larger diameter columns. The ability to confirm the presence of a suspected tin complex by inspecting the emission of tin is a feature of this method not available in others. Finally, although not mentioned in this work, a few days before beginning this work the instrument was used to detect for S, N, and P containing compounds in extracts from oil contaminated water with no modifications made to the instrument between studies.

ACKNOWLEDGEMENTS

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TABLE 1. Concentrations of butyltin compounds in selected fish samples.

Location/ Sample	$BuSn^{3+}$ (4.97) (min)	Bu_2Sn^{2+} (6.18) (min)	Bu_3Sn^{+} (7.40) (min)
Whitby Harbour, Ontario			
F1	22.0±0.7	36.0±0.3	56.0±2.9
F2	25.1±2.2	25.2±0.2	28.8±0.5
F3	19.4±2.2	42.4±1.2	54.6±1.2
F7	46.8±0.6	109.2±0.6	178.8±0.2
F8	37.2±1.8	102.0±1.2	106.8±1.4
F9	38.4±1.2	85.9±3.1	109.2±6.2
F10	---	57.6±16.3	58.4±3.3
Kingston Harbour, Ontario			
F4	14.2±0.0	24.4±0.3	59.6±2.1
F5	15.8±0.9	21.6±2.9	15.8±0.0
F11	21.6±1.2	14.4±2.1	16.8±1.1
Port Dover Harbour, Ontario			
F6	4.3±0.1	4.3±0.3	40.1±3.6

Concentration Unit: ng/g expressed as Sn (whole fish wet weight);
"---" not detectable; retention time given in brackets in min.

TABLE 2. Concentrations of Butyltin compounds in selected sediment samples.

Location/ Sample	$BuSn^{3+}$ (4.97) (min)	Unknown (5.20) (min)	Unknown (5.30) (min)	Bu_2Sn^{2+} (6.15) (min)	Bu_3Sn^{+} (7.40) (min)
Port Dover Harbour, Ontario					
S1	18.8±1.7	122.0±7.6	128.3±9.2	97.0±0.9	106.4±2.9
S2	15.5±1.9	161.2±2.7	158.1±1.1	62.1±2.3	58.9±11.4
S3	58.5±7.9	120.0±4.0	141.5±6.5	67.7±2.6	147.7±11.5
S7	---	126.0±9.1	104.4±9.0	---	36.0±4.1
S8	35.4±2.0	127.4±3.4	145.1±3.2	36.0±2.4	46.8±9.2
S9	---	21.6±1.8	59.2±1.9	21.6±2.2	18.0±2.4
S10	---	86.4±1.9	97.2±5.2	---	18.0±1.3
S11	---	115.2±1.8	126.0±13.1	79.2±2.9	86.4±4.5
Wheatley Harbour, Ontario					
S4	---	---	---	---	9.2±1.2
S5	---	---	---	---	18.5±0.4
S6	---	---	---	21.6±1.7	64.8±5.0

Concentration Unit: ng/g as Sn (dried wt.);
"---" not detectable; retention time given in brackets in min.

CAPTIONS FOR FIGURES

Fig. 1. Effect of make up gas flow rate on the response to the butyltins.

Fig. 2. Response to butyltin compounds as a function of concentration, shown for two make up gas flow rates.

Fig. 3. Typical chromatogram of standard butyltin solution of 0.2 ng/uL.

Fig. 4. Emission spectra of Et3BuSn, showing the expected tin emission lines at 300.9 and 303.4 nm with background correction[22].

Fig. 5. Typical emission chromatogram from a fish sample.

Fig. 6. Typical emission chromatogram of a sediment sample.

Fig. 7. Emission spectra of eluting peak at 5.29 min showing anticipated tin lines at 300.9 and 303.4 nm (with background correction[22]).

FIGURE 1

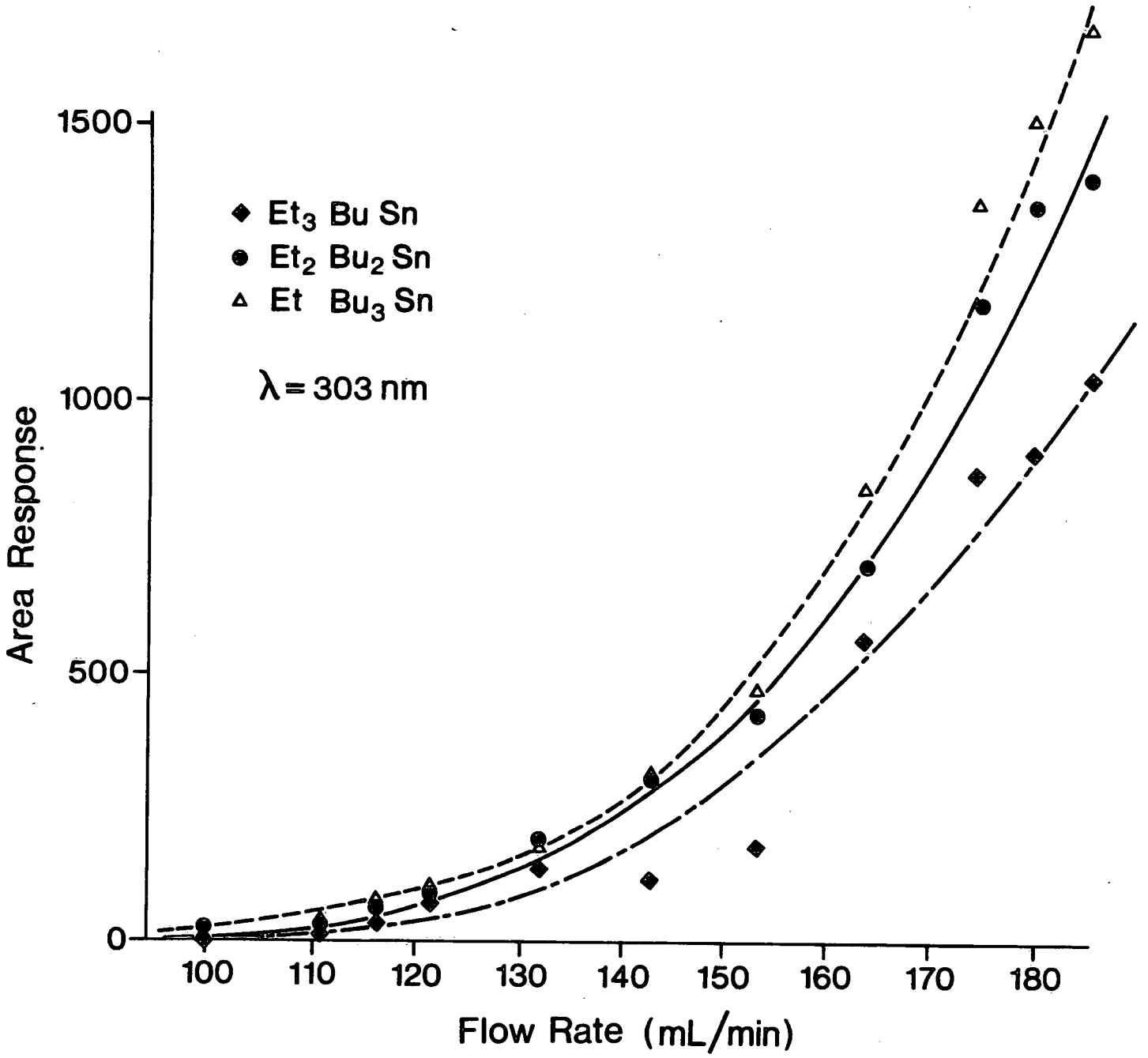

1500
1000
500
0
Area Response
◆ Et3 Bu Sn
● Et2 Bu2 Sn
△ Et Bu3 Sn
λ = 303 nm
100
110
120
130
140
150
160
170
180
Flow Rate (mL/min)

FIGURE 2

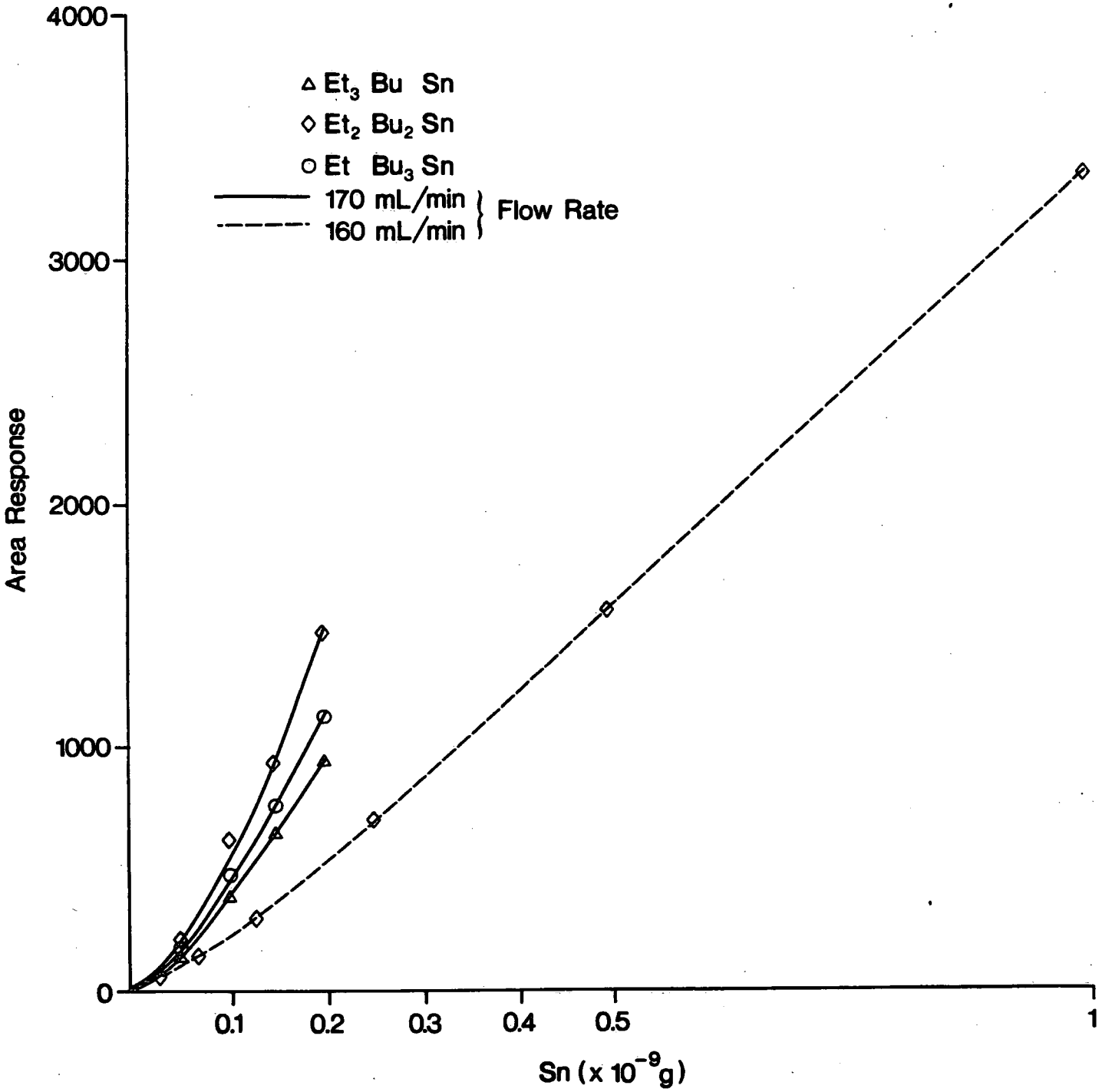

4000
3000
2000
1000
0
Area Response
△ Et_3 Bu Sn
◇ Et_2 Bu_2 Sn
○ Et Bu_3 Sn
170 mL/min
160 mL/min
Flow Rate
0.1
0.2
0.3
0.4
0.5
1
Sn (x 10^{-9} g)

FIGURE 3

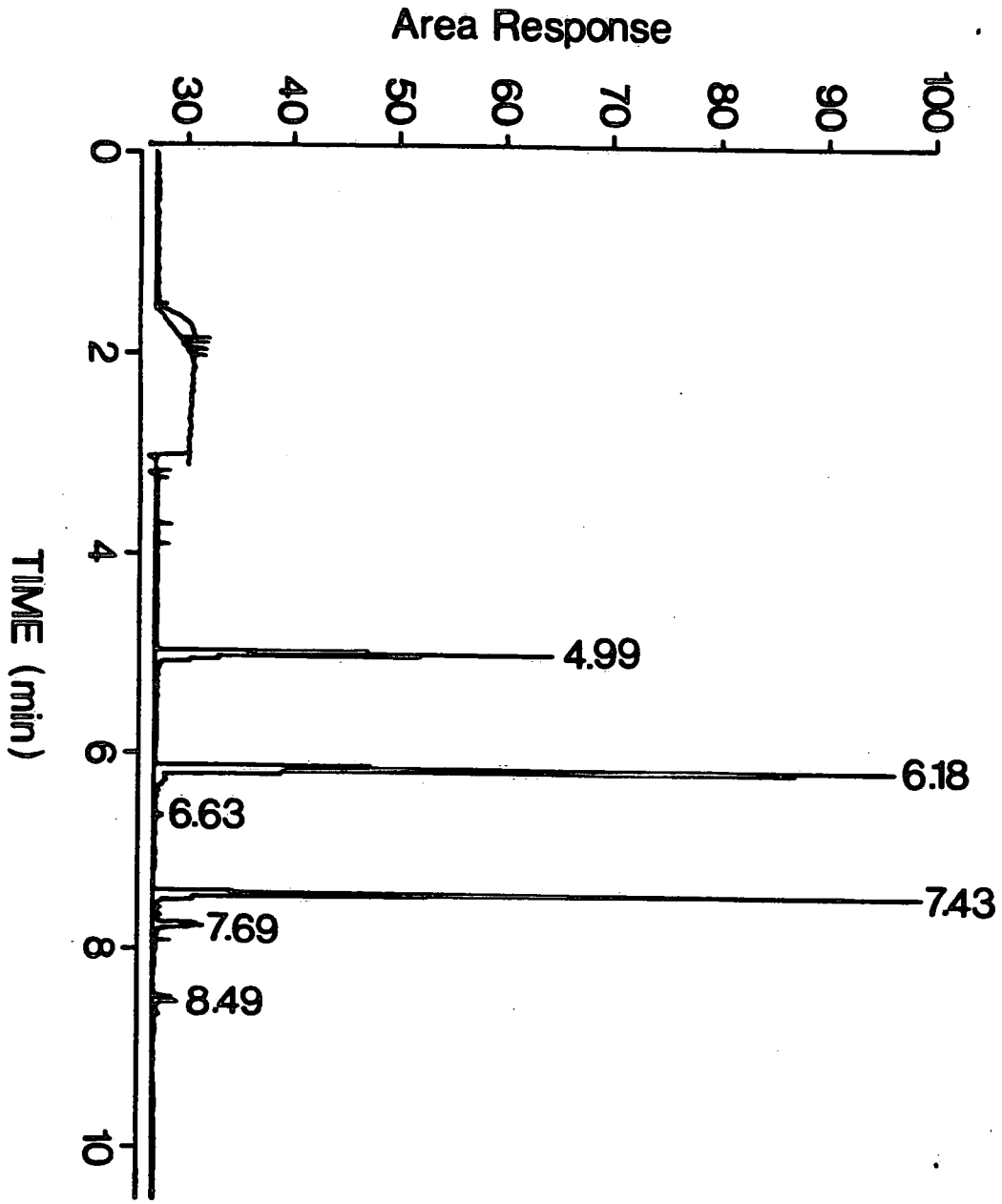

Area Response
30
40
50
60
70
80
90
100
0
2
4
6
8
10
TIME (min)
4.99
6.18
6.63
7.43
7.69
8.49

FIGURE 4

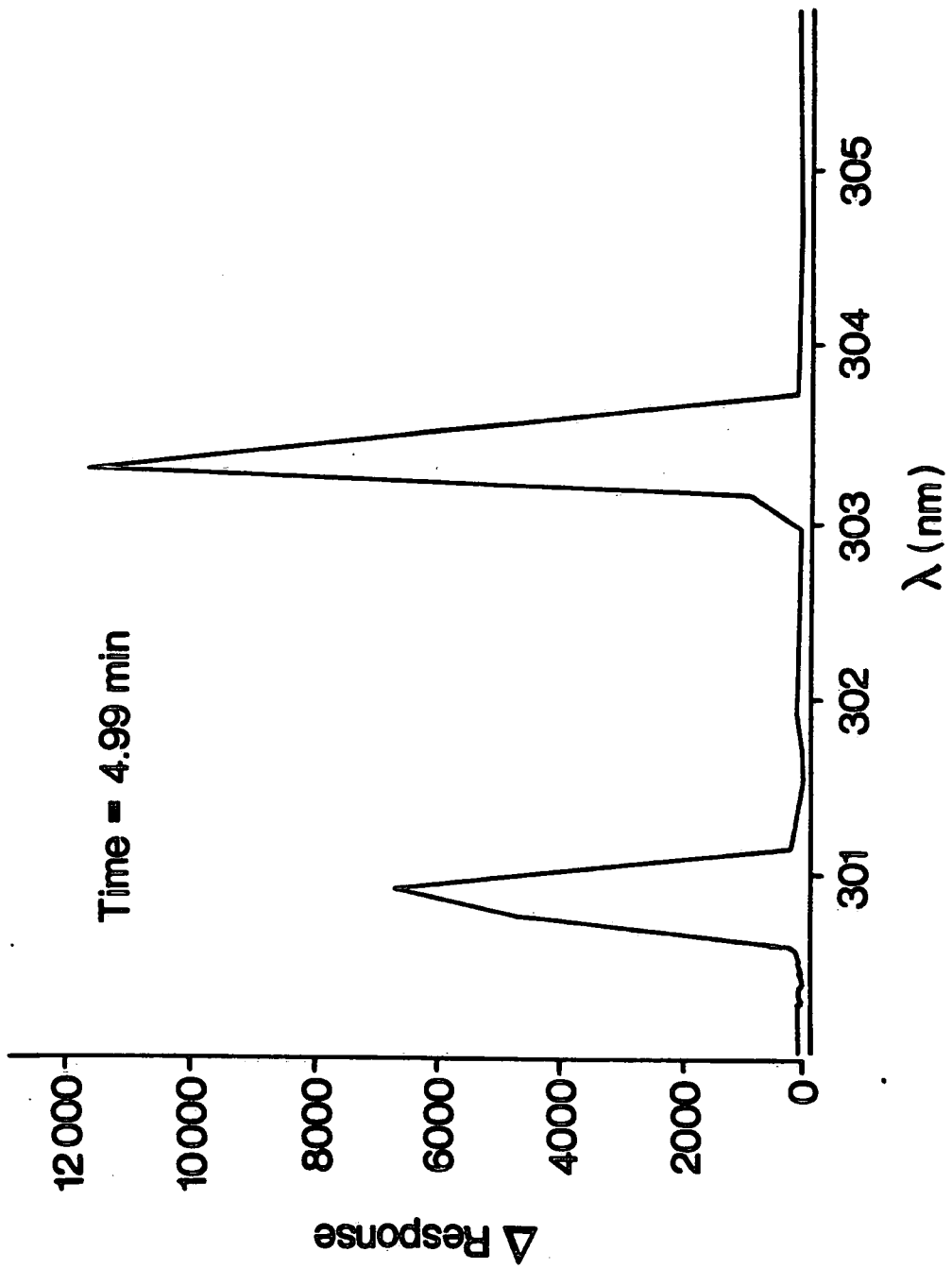

Time = 4.99 min
Δ Response
12000
10000
8000
6000
4000
2000
0
301
302
303
304
305
λ (nm)

FIGURE 5

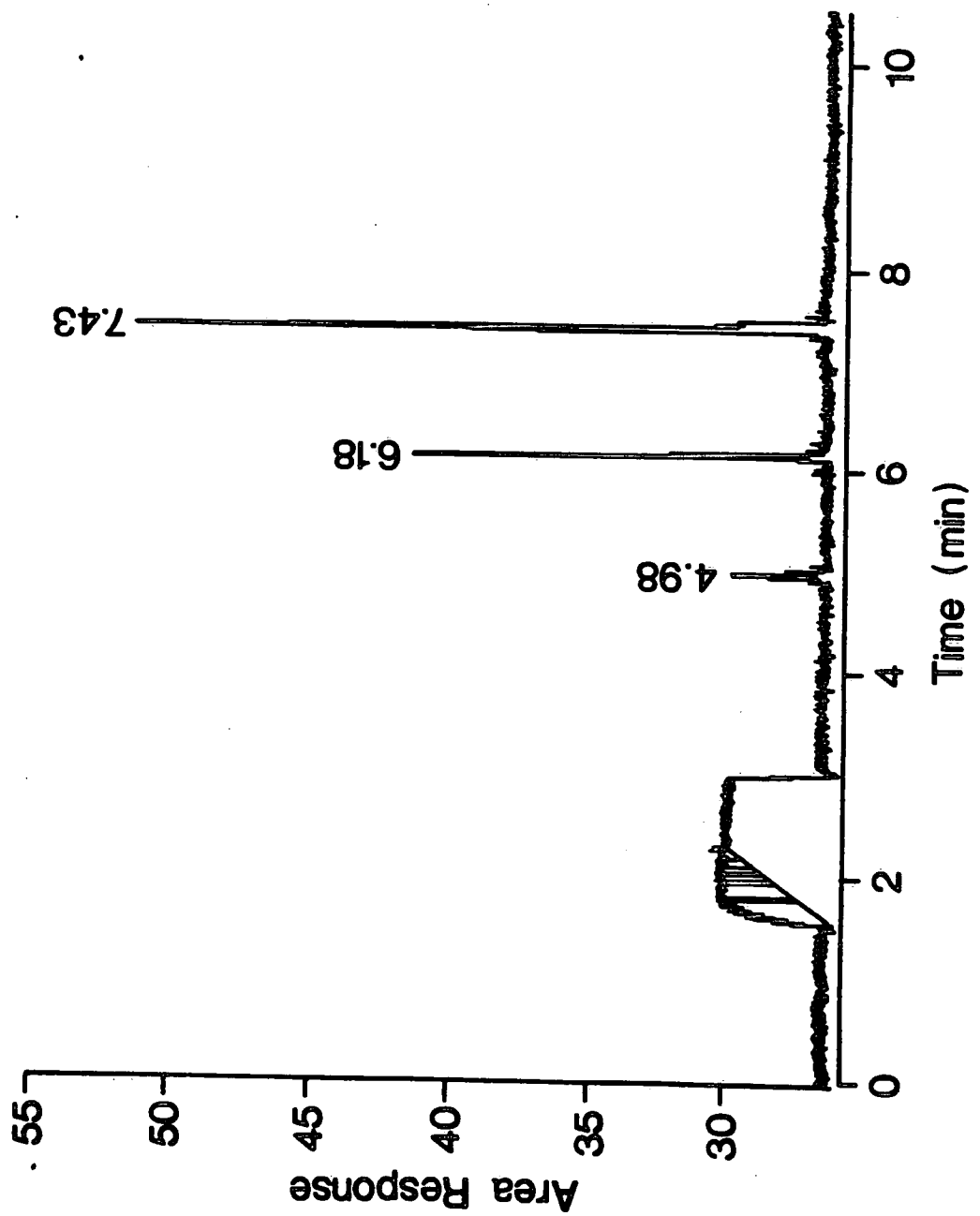


FIGURE 6

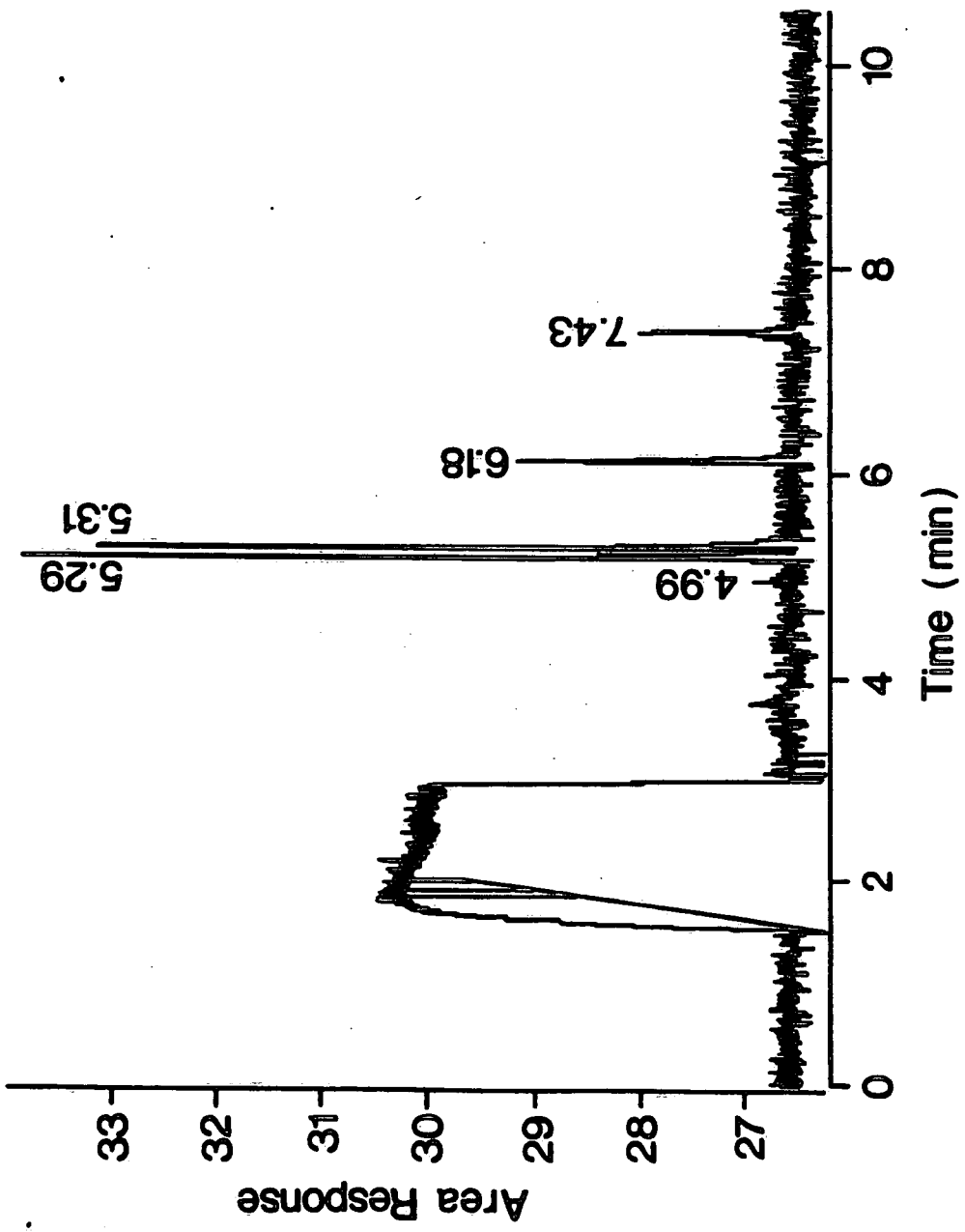
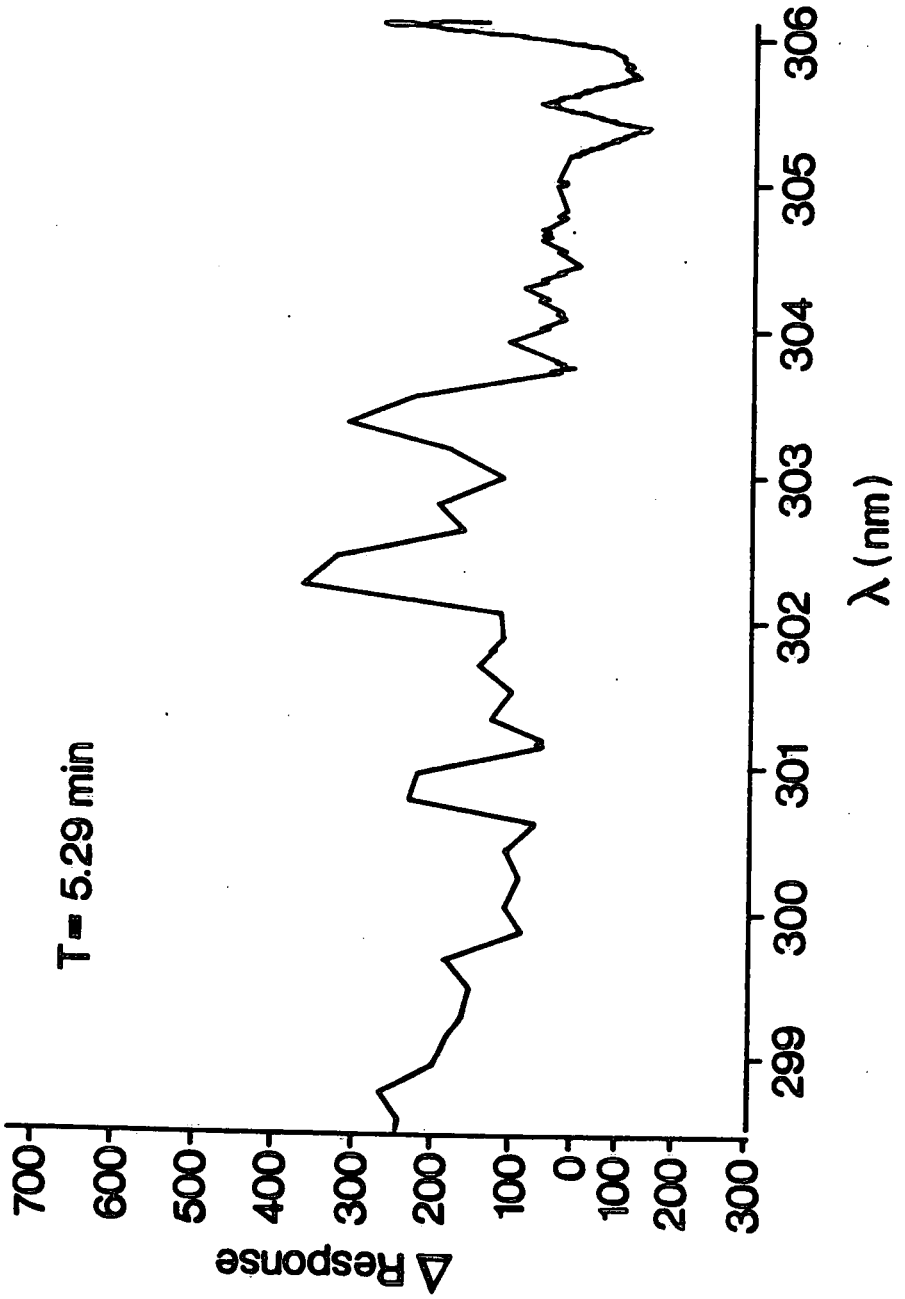
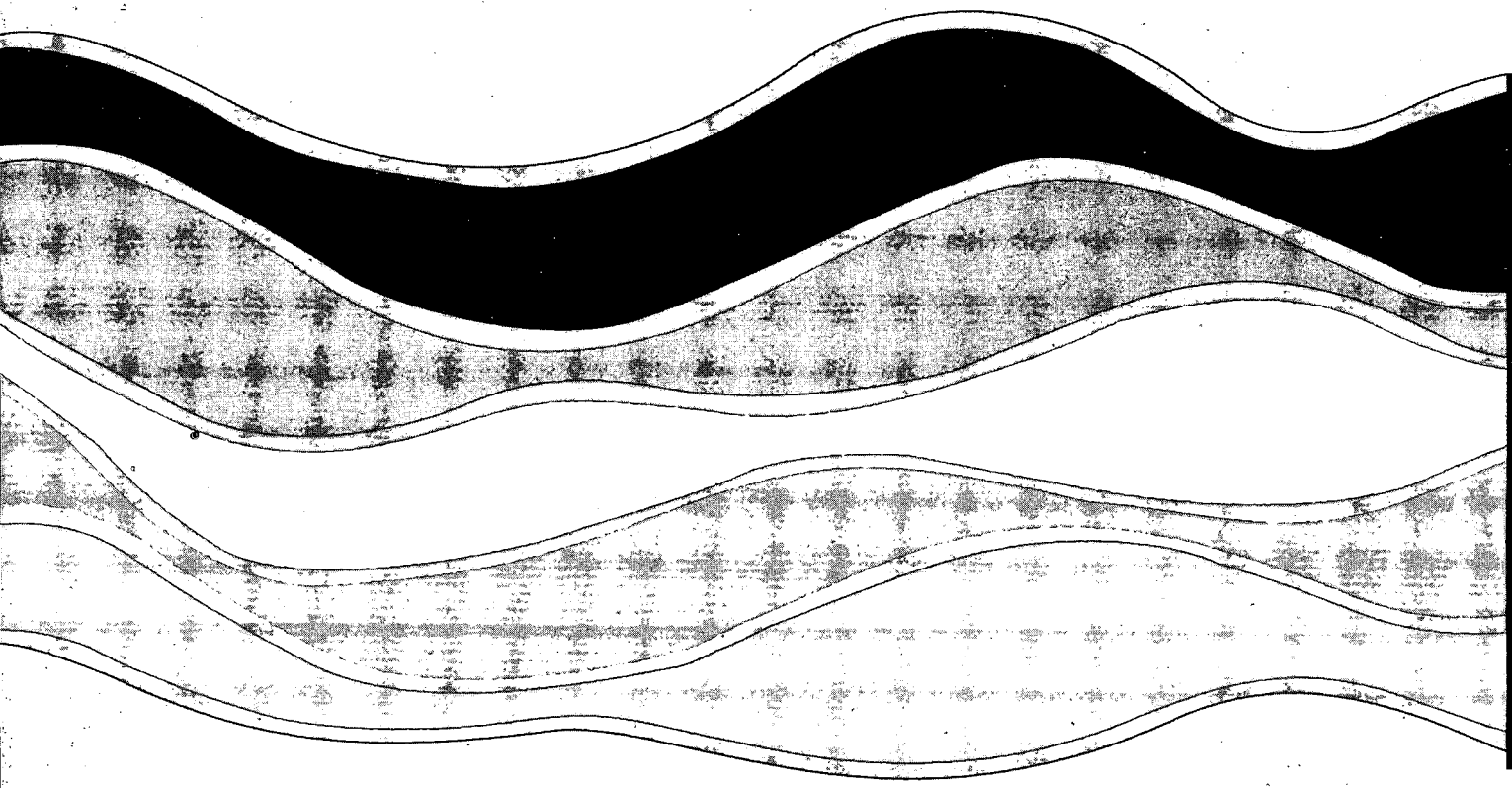

Area Response
33
32
31
30
29
28
27
0
2
4
6
8
10
Time (min)
4.99
5.29
5.31
6.18
7.43

FIGURE 7


T = 5.29 min
Δ Response
700
600
500
400
300
200
100
0
100
200
300
299
300
301
302
303
304
305
306
λ (nm)



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