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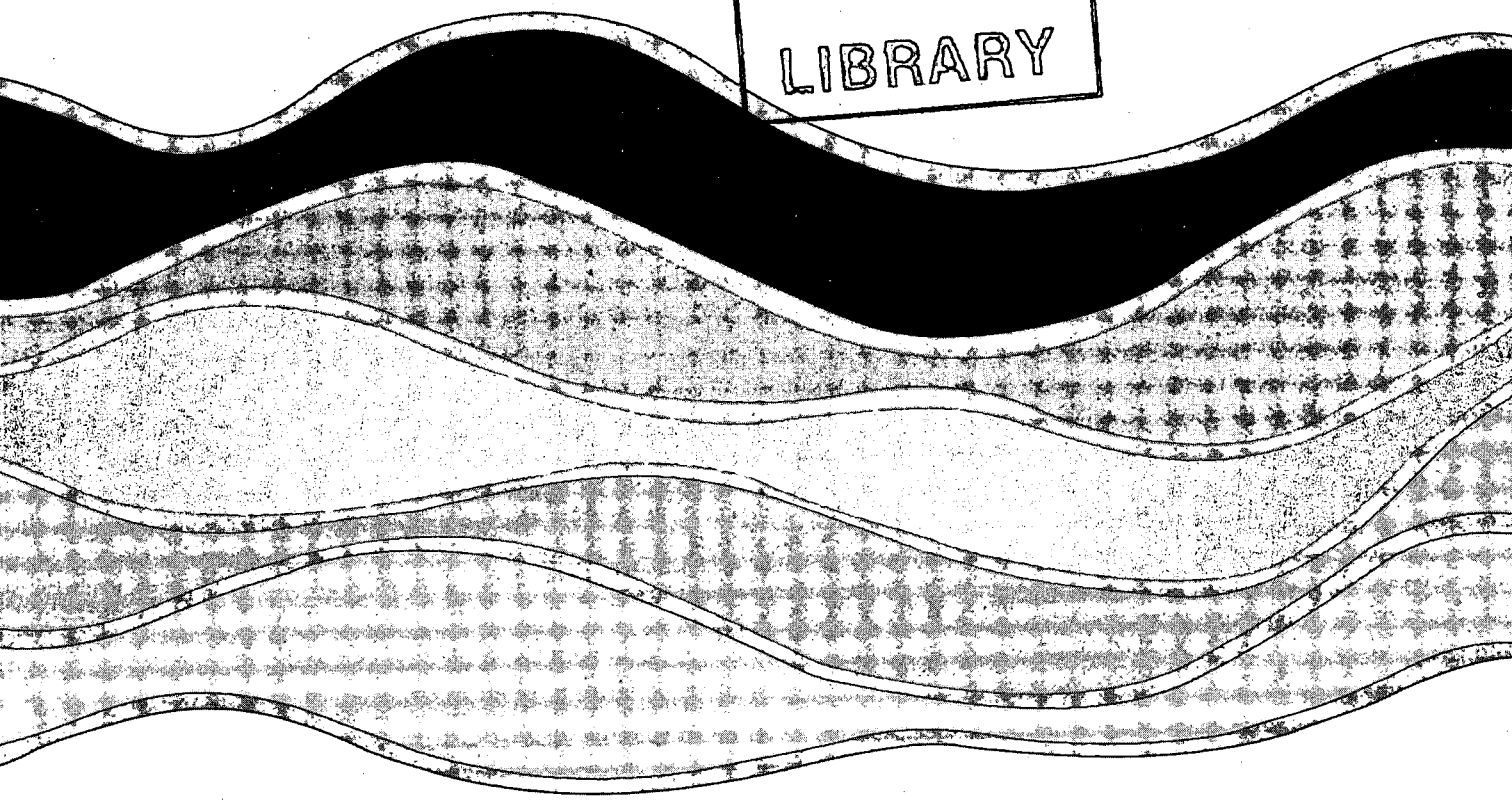

IMPROVEMENT OF THE DETECTION LIMITS OF DIDECYLDIMETHYLAMMONIUM CHLORIDE IN EFFLUENT AND SEDIMENT SAMPLES

H.B. Lee and T.E. Peart

NWRI Contribution No. 94-56

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MANAGEMENT PERSPECTIVE

In response to a request from Integrated Programs Branch, C&P, Environment Canada, Pacific and Yukon Region, methods for the determination of an anti-sapstain chemical, didecyldimethylammonium chloride (DDAC), in effluent and sediment samples have been optimized. Using proven technology, the detection limit of DDAC in effluents was improved by a factor of ten. Recommendations to enhance the recovery of DDAC and to eliminate potential analytical errors were also included. This research was funded by the Fraser River Action Plan.

SOMMAIRE À L'INTENTION DE LA DIRECTION

En réponse à une demande de la Direction des programmes intégrés de C et P, Environnement Canada, Région du Pacifique et du Yukon, on a optimisé des méthodes pour le dosage d'un produit chimique utilisé pour la lutte contre la décoloration de l'aubier, le chlorure de didécyldiméthylammonium (DDAC), dans des échantillons d'effluents et de sédiments. À l'aide d'une technologie éprouvée, on a amélioré la limite de détection du DDAC dans des effluents par un facteur 10. On a également fait des recommandations pour améliorer la récupération du DDAC et pour éliminer des erreurs analytiques possibles. Ces travaux de recherche étaient financés par le Plan d'action du Fraser.

ABSTRACT

Based on an earlier procedure developed by C&P Laboratory Services, Pacific & Yukon Region, Vancouver, a method for the determination of didecyldimethyl-ammonium chloride (DDAC) in effluents was optimized and validated. Using a nitrogen-phosphorous detector, the detection limit of DDAC in the present procedure is 1 μg/L, a 10-fold improvement over the original method. For better recovery of DDAC from effluents, Rexonic was used to minimize its adsorption on active surface and ammonium chloride was added to enhance the extractability of this soluble salt. The mean recovery of DDAC in spiked water samples of 1 μg/L was ca. 95% with a relative standard deviation of less than 4%. Mean recoveries from spiked sediment samples were 60% and 54% at 1 and 0.1 μg/g levels. Confirmation of DDAC in sample extracts was achieved by a Mass Selective Detector and the three characteristic ions (m/z 184, m/z 185 and m/z 311) were monitored. A potential systematic error causing biased high results was identified when the quantitation standard was prepared in pure acetone. Preserved water samples spiked to 1 μg/L of DDAC were stable over the 28-day storage period.

RÉSUMÉ

En se basant sur une méthode antérieure développée par les Services de laboratoire de Conservation et Protection, Région du Pacifique et du Yukon, Vancouver, on a optimisé et validé une méthode pour le dosage du chlorure de didécyldiméthylammonium (DDAC) dans les effluents. À l'aide d'un détecteur azote-phosphore, on a obtenu une limite de détection de 1 μg/L pour le DDAC avec la méthode actuelle, soit une amélioration d'un ordre de grandeur par rapport à la méthode initiale. Pour une meilleure récupération du DDAC des effluents, on a utilisé du Rexonic pour minimiser l'absorption sur la surface active et on a ajouté du chlorure d'ammonium pour améliorer l'extractibilité du sel soluble. La récupération moyenne du DDAC dans des échantillons d'eau enrichis de 1 μg/L était d'environ 95 %, avec un écart type relatif de moins de 4 %. Les récupérations moyennes à partir d'échantillons de sédiments enrichis étaient de 60 et de 54 % à des teneurs de 1 et de 0,1 μg/g. On a obtenu une confirmation des teneurs en DDAC dans les extraits des échantillons à l'aide d'un discriminateur de masse et les trois ions caractéristiques (m/z 184, m/z 185 et m/z 311) ont été surveillés. Une erreur systématique possible entraînant des résultats trop élevés a été signalée quand la solution étalon de dosage était préparée avec de l'acétone pure. Les échantillons d'eau préservés enrichis à 1 μg/L de DDAC étaient stables pendant toute la période de stockage de 28 jours.

INTRODUCTION

Anti-sapstain chemicals are used to minimize wood discoloration derived from fungal reactions. In the past, pentachlorophenol (PCP) and its derivatives were traditionally used by the forest product industry for the treatment of wood. Because of the toxicity of PCP to humans and fish, other alternatives including azaconazole, copper-8-quinolinolate, didecyldimethylammonium chloride (DDAC), 3-iodo-2-propynyl butyl carbamate (IPBC), borax and 2-(thiocyanomethylthio)benzothiazole are being used as the replacements for PCP [1]. Among these substances, DDAC is being used in considerable amounts as an anti-sapstain chemical in British Columbia and has been identified as a contaminant in the Fraser River and its tributaries.

DDAC is presently used in the following four anti-sapstain formulations, namely, TimberCote II (20% DDAC), TimberCote 2000 (28% DDAC), F2 (11.4% DDAC, 16.8% disodium octaborate tetrahydrate), and NP-1 (65% DDAC, 7.7% IPBC). It is a quartenary ammonium salt and very soluble in water. There is no measurable vapour pressure and no volatilization for this salt. Preliminary results indicated that the oral LD_{50} of DDAC in Wistar rats was 360 mg/kg and it is a severe eye and skin irritant. Acute static toxicity tests yielded 96-hour LC_{50} values of 1.0 mg/L to salmon, 0.069 mg/L to mysid shrimp and 0.32 mg/L to bluegill sunfish [2]. The octanol-water partition coefficient (K_{ow}) was estimated to be either zero or negative and thus bioconcentration is not expected to occur.

The environmental effects and impacts of DDAC as a contaminant in Fraser River and its tributaries have been studied under the Fraser River Action Plan (FRAP) for some time. Methods for the determination of DDAC in effluent and sediment samples were developed by Laboratory Services, Conservation and Protection, Pacific & Yukon Region, Environment Canada [3]. The final analysis was based on the thermal decomposition of DDAC in a heated injection port to form tertiary amines and alkyl

chlorides. Using capillary column gas chromatography and nitrogen-phosphorus detection, the published detection limit was 10 μg/L for effluent samples and 0.05 μg/g for sediment samples. While the methods are good and have been used for routine analysis, the detection limits do not meet the requirement for the measurement of ambient concentrations of DDAC for some programs in the FRAP. The aim of this study is to improve the detection limits for DDAC in effluent and sediment samples as well as to define the precision and accuracy of the method at such levels. After consultation with the officials from the Integrated Programs Branch, Pacific and Yukon Region, our target detection limit for DDAC in effluent samples was set at 1 μg/mL. Because of the availability of equipment in our laboratory, only gas chromatographic techniques for the analysis of DDAC were evaluated.

EXPERIMENTAL

Reagents and chemicals

All solvents were distilled-in-glass grade supplied by Burdick and Jackson. Concentrated hydrochloric acid (J.T. Baker), formaldehyde (37% w/w solution, J.T. Baker) and ammonium chloride (Fisher) were all ACS Reagent grade. Anhydrous sodium sulfate (Analytical Reagent grade) was a product of BDH. Bardac 2280 (80% DDAC) was provided by Lonza Inc., Long Beach, California (1-310-537-0451). Didecyldimethyl-ammonium bromide (DDAB, >97%), didecylmethylamine (DDMA, >90%), and decyldimethylamine (DMDA, >98%) were purchased from Fluka Chemika-BioChemika. Rexonic N25-7, a multi-component nonionic surfactant in the chemical form of alkyl polyoxyethylene glycol ether, was obtained from Texaco Chemical Canada, Guelph, Ontario (1-800-561-6625). A 2,000 mg/L solution of Rexonic was prepared by dissolving 2.00 g of this material in 1 L of distilled and deionized water. An acidified methanol solution was made up by careful addition of 6 mL of concentrated hydrochloric acid to 150 mL of methanol.

Preservation of samples

Effluent and sediment samples were preserved as per original method. Briefly, 5 mL of Rexonic N25-7 solution (2,000 mg/L) and 10 mL of formaldehyde solution (37%) were added to a 1 L effluent at the time of sampling. Similarly, 2.5 mL of the Rexonic solution and 5 mL of formaldehyde were added to each 100 g of sediment collected. The samples were kept at 4°C and analyzed as soon as possible.

Extraction of water samples

To each 1 L sample in a 40 oz. (1.14 L) glass bottle, 50 mL of dichloromethane (DCM) and 5 g of ammonium chloride were added. The sample was vigorously stirred with a magnetic stirring bar for 30 min and then the entire sample was transferred to a 2 L separatory funnel. After phases separated, the lower organic layer was drained into a 250 mL round bottom flask. The water sample was returned to the original container and the extraction was repeated twice with two 50 mL aliquots of DCM. The combined extract was dried over 2 to 3 cm of anhydrous sodium sulfate in a sintered-glass filter funnel into another 250 mL round bottom flask and rotary evaporated under reduced pressure to just dryness in a 45°C bath. The residue was then quantitatively transferred to a calibrated test tube with four 1 mL aliquots of acetone. The sample volume was finally reduced to 1 mL by nitrogen evaporation in a 45°C bath for GC and GC-MS analysis.

To quantitate each set of DDAC samples in this work, a 1 L organics free water containing the same amounts of Rexonic and formaldehyde solutions as the samples were extracted with DCM as described above. Fifty μL (or an appropriate amount) of the 20 μg/mL DDAC solution was added to the acetone extract in a calibrated test tube and the volume was adjusted to 1.0 mL for final analysis. See later discussion.

Stability study of spiked water samples

One litre aliquots of deionized organics-free water were spiked to a DDAC level of 1 μg/L. Immediately after spiking, 5 mL of the 2,000 mg/L Rexonic solution and

10 mL of formaldehyde were added to each sample before they were stored at 4°C in the dark. Triplicate samples were analyzed immediately, as well as at day 4, day 7, day 14 and day 28.

Extraction of sediment samples

A wet sediment sample, typically 15 g, was air dried to constant weight for moisture content determination. Another wet sediment sample which was equivalent to a dry weight of 10 g was weighed into a 250 mL Erlemeyer flask. To this sample, 5 mL of the Rexonic solution and 50 mL of the acidified methanol solution were added. The sample was stirred with a magnetic bar for 1 h. After the sediment settled, as much of the supernatant as possible was filtered through a Buchner funnel with a piece of Whatman No. 1 filter paper and the filtrate was collected in a 250 mL vacuum filtration flask. The sediment was extracted twice again with 25 mL aliquots of the acidified methanol solution for 15 min each. At the end of the third extraction, the entire suspension was filtered through the same funnel under reduced pressure. The combined methanoic extract was filtered through a layer of anhydrous sodium sulfate and then evaporated to 10 mL or less with a rotary evaporator and a water bath at 55°C. The concentrated extract was transferred to a 250 mL separatory funnel containing 5 mL of the Rexonic solution and 200 mL of a 5% ammonium chloride solution. DDAC was then back extracted into the organic phase by shaking with three 25 mL aliquots of DCM for 1 min each. The combined DCM solution was dried with anhydrous sodium sulfate and rotary evaporated in a 45°C bath to just dryness. The residue was reconstituted in acetone and adjusted to a final volume of 1.0 mL as per effluent samples.

Chromatographic analysis of sample extracts

A Hewlett-Packard 5890 Series II Plus GC equipped with a nitrogen-phosphorus detector (NPD), a Model 7673 autosampler and a 0.25 mm ID x 30 m HP Ultra-2 column was used for GC-NPD analysis. The NPD flow rates were: hydrogen, 3.5 mL/min (30 psi), air 100 mL/min (65 psi) and helium make-up gas 25 mL/min (30 psi). The carrier gas (helium) was maintained at a constant flow of 1.2 mL/min

throughout the run by the electronic pressure controller. The injection port and detector temperatures were 325°C and 300°C, respectively. The following temperature program was used: initial oven temperature, 70°C (hold for 1 min), ramp rate 1, 30°C/min (from 70 to 140°C), ramp rate 2, 10°C/min (from 140 to 240°C), and the final temperature was held for 4 min. One microlitre samples were injected in the splitless mode and the splitless time was 1 min.

Another Hewlett-Packard Series II GC equipped with a Model HP 5972A Mass Selective Detector (MSD) was used for the confirmation of DDAC in sample extracts. The MSD was operated in electron-impact ionization (EI), selected ion monitoring (SIM) mode. Three ions, m/z 184, m/z 185 and m/z 311, were monitored and a solvent delay of 6 min was used. The electron energy was 70 eV and the electron multiplier was set at 400 V above the autotune value. Chromatographic conditions were similar to the GC-NPD work described above.

RESULTS AND DISCUSSION

Chromatographic and Mass Spectral Properties of DDAC

Quartenary ammonium salts are known to decompose in a heated GC injection port to yield tertiary amines as degradation products [4]. In the case of DDAC, both didecylmethylamine (DDMA) and decyldimethylamine (DMDA) are formed since two different alkyl groups are present in the parent salt. (The other stoichiometric degradation products of DDAC are decyl chloride and methyl chloride, both of which are not used for any qualitative or quantitative purposes in this study.) A NPD is used in the existing method to analyze samples of DDAC. This detector is well suited for environmental samples because of its selectivity and enhanced sensitivity toward nitrogen-containing compounds such as amines. Since DDAC is not observed under normal GC conditions, DDMA, the more predominant degradation product, is chosen for the quantitation of the parent compound.

The response of a DDAC standard using nitrogen-phosphorus detection demonstrated a dependency on several parameters. Repeated 1 μL injections of a 1 ng/μL DDAC solution in acetone at injection port temperatures of 250°, 275°, 300° and 325°C indicated increased detector response with increasing injector temperature. If the peak area observed for DDMA at an injection port temperature of 250°C was 100, the areas for the same standard injected at 275°, 300° and 325°C were, 129, 151 and 174, respectively. Injector temperatures higher than 325°C were not tested since excessive septum bleed and thermal stripping of the GC column stationary phase at the inlet end would be expected.

The NPD response of DDAC in pure acetone was fairly linear for concentrations of 10, 5, 1, 0.5, and 0.2 ng/μL (Table 1 and Figure 1) and the correlation coefficient (r) was 0.9993. It was, however, quite obvious from Table 1 that the response of DDAC dropped off at the lowest concentration. Meanwhile, the solvent used to prepare the injection solution also played a role in the response of DDAC. For example, a 50% or more reduction in detector response was observed when *iso*-octane instead of acetone was used as injection solvent. In contrast, the detector response increased by as much as 30% (see Table 1, Figure 1 and later discussion) when the solvent acetone also contained the coextractives coming from Rexonic, a reagent used to minimize the loss of DDAC in the procedure due to adsorption. Thus, biased high results are likely to be observed for the preserved water samples if the DDAC quantitation standard is prepared in acetone alone.

Under electron-impact ionization (EI) conditions, two peaks were observed for DDAC using the Mass Selective Detector operating in the full scan mode. Again, the major and minor peaks were confirmed by authentic standards as DDMA and DMDA, respectively and their mass spectra are given in Figure 2. These spectra were not identical to those given in the original method since the latter were obtained by an ion trap detector which does not produce classical EI spectra. Only three characteristic ions, namely, m/z 311 (M^+), m/z 185, $[M\text{-}C_9H_{18}]^+$ or $[(C_{10}H_{21})(CH_3)_2N]^+$, and m/z 184, [M-

$C_9H_{19}]^+$ or $[(C_{10}H_{21})(CH_3)N{=}CH_2]^+$ were observed for DDMA. The mass spectrum of DMDA is remarkably simple and it consists of a base peak at m/z 58 ($C_3H_8N^+$, a non-characteristic ion), the M^+ ion (m/z 185) and a few other ions of relative abundance of 5% or less. Since the M^+ ions for both DDMA and DMDA are weak (less than 3% relative abundance), they are thus unsuitable for quantitation or confirmation purposes at low levels.

No improvement in sensitivity was observed when DDAC was analyzed on a Hewlett-Packard MS Engine operating in the EI mode. The use of an Atomic Emission Detector (AED) and chemical ionization mass spectrometric techniques for the final analysis of DDAC were not evaluated because of potential availability problems of these instruments in some laboratories.

Extraction of effluent samples at 1 μg/L level

Since the NPD can easily detect 1 ng of DDAC, by using a concentration factor of 1,000, one should be able to achieve a detection limit of 1 μg/L in effluents provided the recovery is close to quantitative. To test this hypothesis, replicate water samples spiked to 1 μg/L of DDAC were extracted in the presence of Rexonic and formaldehyde. When the sample extracts were quantitated against a DDAC standard prepared in pure acetone, recoveries over 100% were consistently obtained by using NPD detection. These results were further confirmed by GC-MSD, indicating that the high results were not due to interference or artifacts. A check of the Rexonic and formaldehyde reagents used for sample preservation did not show any blanks. The apparently high recovery was later found to have resulted from the enhanced detector response for DDAC in the presence of the coextractives coming from the Rexonic reagent in the sample. Presumably, these coextractives induced a more complete transfer (less adsorption) of DDAC from the injection port to the column. Using a DDAC standard prepared in the Rexonic blank as described in the experimental section, the corrected recovery of DDAC from water spiked at 1 μg/L ranged from 84 to 93%.

The addition of 5 g of ammonium chloride to the effluent sample prior to extraction produced a slight (5 to 10%) improvement on the recovery of DDAC. The use of a salt to enhance the extractability of polar organics from water samples is well known. Therefore it is not surprising that ammonium chloride, with a structure similar to DDAC, improves the recovery of the anti-sapstain chemical from effluents.

Since it is too tedious to prepare a series of DDAC quantitation standards in the presence of the coextractives from Rexonic for each set of samples, an alternative is to apply a correction factor to the DDAC concentrations determined by using DDAC quantitation standards prepared in pure acetone. As the detector response is linear (Figure 1) for DDAC over the concentration range from 10 to 0.2 ng/μL, an average correction factor for the response of DDAC with and without the Rexonic factor can be determined from similar results as given in Table 1.

A typical NPD chromatogram of an extract for a water sample previously spiked to 1 μg/L of DDAC is shown in Figure 3. The peak with a retention time of 16.185 min is DDMA. Because of the coextractives derived from the matrix and particularly the Rexonic and formaldehyde reagents, a full scan GC-MS analysis of a water extract produced a very complicated chromatogram. The DDAC peak was often hidden under other interfering peaks from the same sample so that identification was virtually impossible. In contrast, confirmation of DDAC in sample extracts could easily be achieved by monitoring the three characteristic ions of DDMA (i.e. m/z 184, m/z 185 and m/z 311, retention time 15.12 min) as illustrated in Figure 4. Note that all characteristic ions including M^+ were observed and quantitated at an injection level of 1 ng/μL. The presence of DDAC was confirmed if all three ions were present at the right retention time and the areas of those ions were in the expected ratios. Because the M^+ ion is weak, it may not be observable for DDAC samples lower than 1 μg/L unless a concentration factor higher than 1,000 is used.

The stability of DDAC in water, spiked to 1 μg/L, preserved with Rexonic and formaldehyde and stored at 4°C in the dark, was also briefly studied. Samples were determined in triplicate at day 0, day 4, day 7, day 14, and day 28. Because of time limitation, this preservation study could not be further continued. The results (Table 2) indicated no evidence of loss or degradation for DDAC at the above concentration during the 28-day storage period.

Further improvement for the detection limit of DDAC in effluent is likely to be possible through an increase in concentration factor. This can be achieved by an increase in the sample size and/or a decrease in the final volume. However, additional investigation of the method's performance at such levels is required.

Extraction of sediment samples

The stated detection limit for DDAC in sediment samples was 0.05 μg/g. This number is dubious since validation data were only available at 1 μg/g, or 20 times the detection limit. Based on the 10 μg/L detection limit and a concentration factor of 250 for DDAC in the original method for effluent samples, the calculated detection limit for sediment would have been 0.5 μg/g for a 10 g sample (dry weight) and a concentration factor of 5.

For the extraction of sediment samples, we were unable to evaporate the methanoic extract to dryness in a 45°C bath using a rotary evaporator as described in the original procedure. Raising the bath temperature to 55°C and adding anhydrous sodium sulfate did not help. Thus, a partitioning step with 5% w/v solution of ammonium chloride and a back extraction into DCM as described before were included. The partitioning step not only removed water in the extract but also eliminated some of the very polar coextractives from the sediment that might interfere with the final analysis. Again, 5 mL of the Rexonic solution was added prior to back extraction to minimize adsorptive losses of DDAC in this process.

Using the present procedure, the mean recoveries of DDAC from spiked sediments were 60% and 54% at 1 and 0.1 μg/g levels, respectively. Since the data were obtained from two different sediments and the recoveries were consistent at two levels of spiking, the low recoveries were not the results of random errors. Although our results were quite a bit lower than those reported in the original method, these numbers were *corrected* for the Rexonic effect described earlier. Also, differences in the sample matrix, such as varying amounts of diatomaceous earth and silicates in the sediments used by the two laboratories, were also likely to be a factor contributing to different recoveries of DDAC. Attempts by using different extraction solvents such as mixtures of acidified DCM and methanol as well as acetone and hexane failed to improve the recovery of DDAC from sediments. The estimated detection limit for sediment, 0.1 μg/g, is similar to the *stated* detection limit of the original method.

Because of the shortage of time, the stability of DDAC in spiked sediment samples was not evaluated for this work.

CONCLUSIONS AND RECOMMENDATIONS

The detection limit of DDAC in effluents can be lowered by a factor of ten through an optimization of the existing procedure. This conclusion was supported by the precision and accuracy data obtained by GC-NPD from fortified samples at 1 μg/L level, confirmation results generated by GC-MSD operating in the selected ion monitoring mode, as well as stability data collected over a 28-day period. Validation results were also generated for sediments spiked to contain 0.1 μg/g of DDAC, a level similar to the detection limit quoted for these samples.

In order to achieve the lower detection limit and avoid potential analytical errors, the following modifications to the original procedure are recommended:

1. Use a concentration factor of 1,000 for effluent samples, i.e. extract a 1 L sample and adjust the extract to a final volume of 1 mL for GC-NPD analysis.

2. For improved extraction efficiency, add 5 g of ammonium chloride to the effluent prior to solvent extraction.
3. Prepare calibration curves for DDAC in acetone with and without the Rexonic coextractives. Determine an average correction factor over this concentration range. For daily analysis, use DDAC standard prepared in pure acetone for the calibration of the NPD and apply the correction factor to calculate the adjusted DDAC concentration in samples.
4. Extract a sediment sample with acidified methanol in the presence of 5 mL of the Rexonic solution. Include a partitioning step to remove water and some polar coextractives in sediment extracts and back extract DDAC with DCM. Add another 5 mL of the Rexonic solution to the aqueous layer before back extraction.
5. Confirm the identity of DDAC by a Mass Selective Detector (or equivalent) in selected ion monitoring mode and monitor the three characteristic ions (m/z 184, m/z 185 and m/z 311) for DDMA, the major thermal degradation product of DDAC.
6. From the stock 1000 μg/mL DDAC standard, prepare an intermediate standard of 20 μg/mL and use it for spiking and preparation of calibration standards at lower concentrations. Prepare a new intermediate solution once a month and all calibration standards just before final analysis to avoid potential losses due to adsorption and degradation.

ACKNOWLEDGMENT

We thank Lonza Inc. and Texaco Chemical Canada for free samples of Bardac 2280 and Rexonic N25-7, respectively.

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2. Material Safety Data Sheet for Bardac 2280, Lonza, 17-17 Rt. 208, Fair Lawn, New Jersey 07410, USA.

3. R.E. Strub, "NPD-Gas Chromatographic, GC/MS Methods for the Determination of Didecyldimethylammonium Chloride in Effluent and Sediment Samples, V2.0, January, 1993", Laboratory Services, Conservation and Protection, Pacific and Yukon Region, Environment Canada.

4. Handbook of Derivatives for Chromatography (1978), edited by K. Blau and G. S. King, Heyden, London, England.

Table 1. Peak area of DDAC at various concentrations by NP detection

ng/µL	A	B
0.20	3728	4194
0.20	3375	4649
0.50	9594	11839
0.50	10073	11870
1.00	18406	23402
1.00	19688	24567
5.00	93441	124020
5.00	101214	122943
10.00	184610	262039
10.00	191973	248578

A = standard prepared in acetone only
B = standard prepared in acetone with Rexonic coextractives

Figure 1

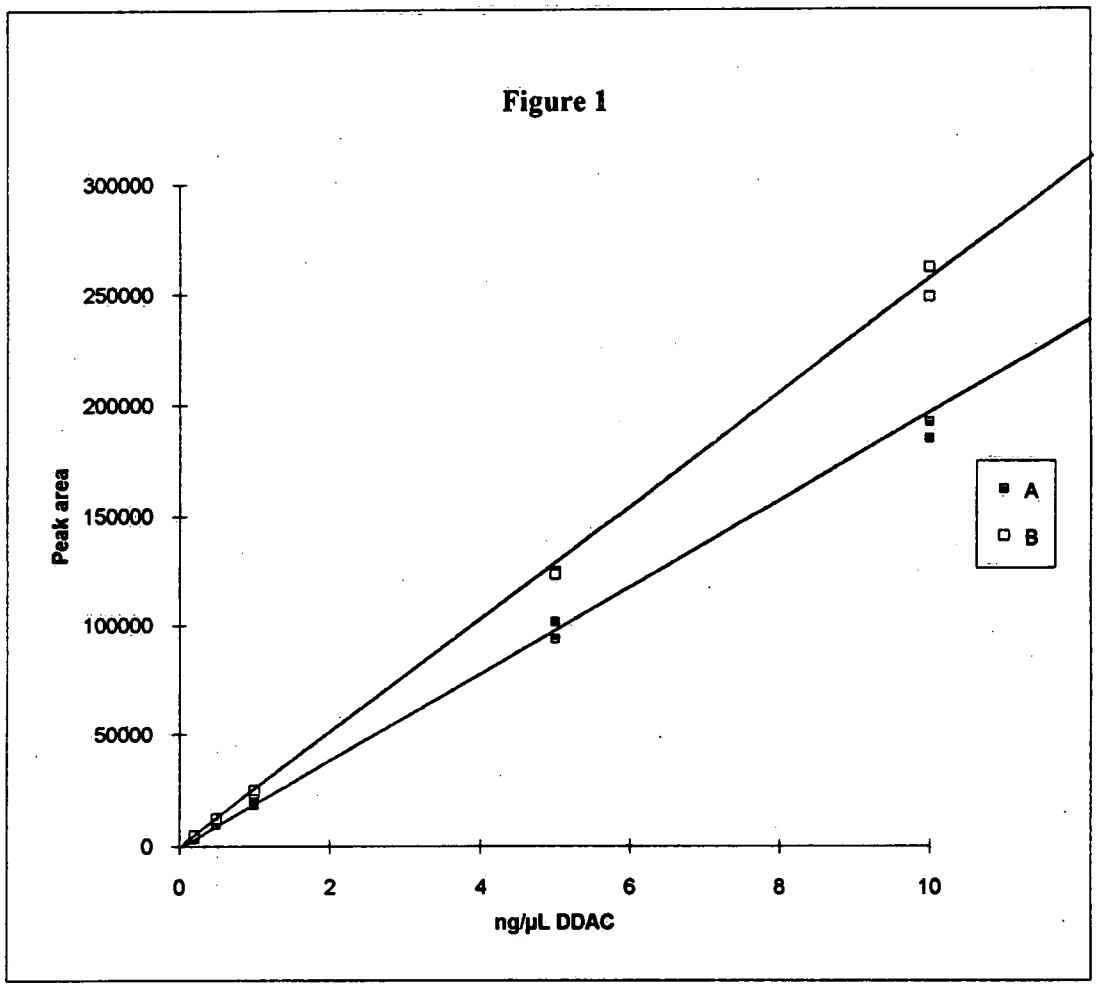
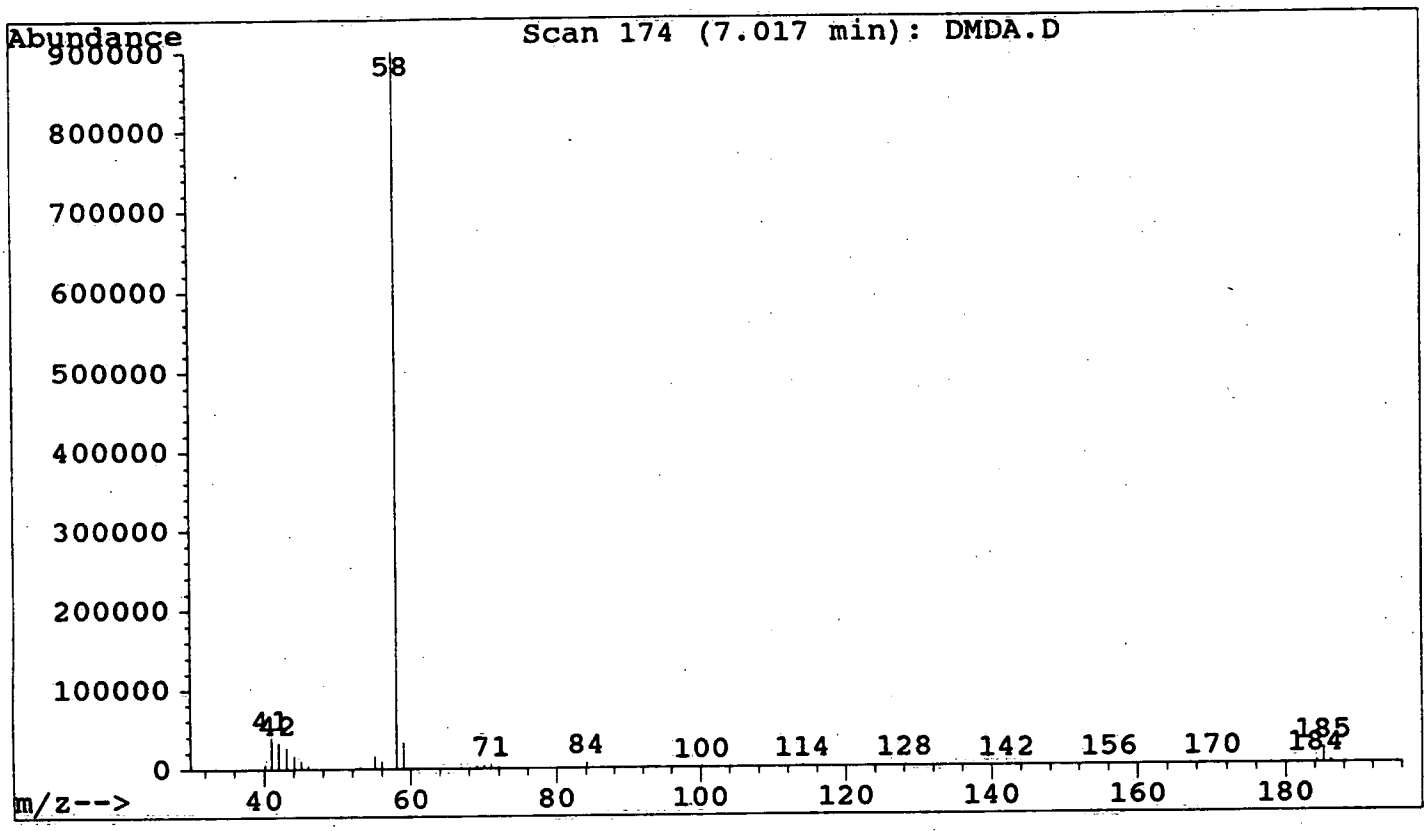


Table 2. Recovery of DDAC in water and sediment samples under various conditions.

Matrix	Spiking level	Storage time	Replicate	Recovery ± S.D.
D.W.*	10 μg/L	none	3	94.1 ± 3.8
D.W.	1.0 μg/L	none	6	95.7 ± 3.3
D.W.	1.0 μg/L	4 days	3	93.4 ± 4.2
D.W.	1.0 μg/L	7 days	3	92.5 ± 4.6
D.W.	1.0 μg/L	14 days	3	95.3 ± 4.2
D.W.	1.0 μg/L	28 days	3	92.8 ± 5.4
Fraser River	1.0 μg/L	none	3	94.1 ± 5.9
Sediment**	1.0 μg/g	none	4	60.3 ± 4.3
Sediment***	0.1 μg/g	none	4	56.4 ± 3.7

* Organics free distilled and deionized water.
** A reference Lake Ontario sediment which is free of DDAC.
*** A reference Lake St. Clair sediment which is free of DDAC.

Figure 2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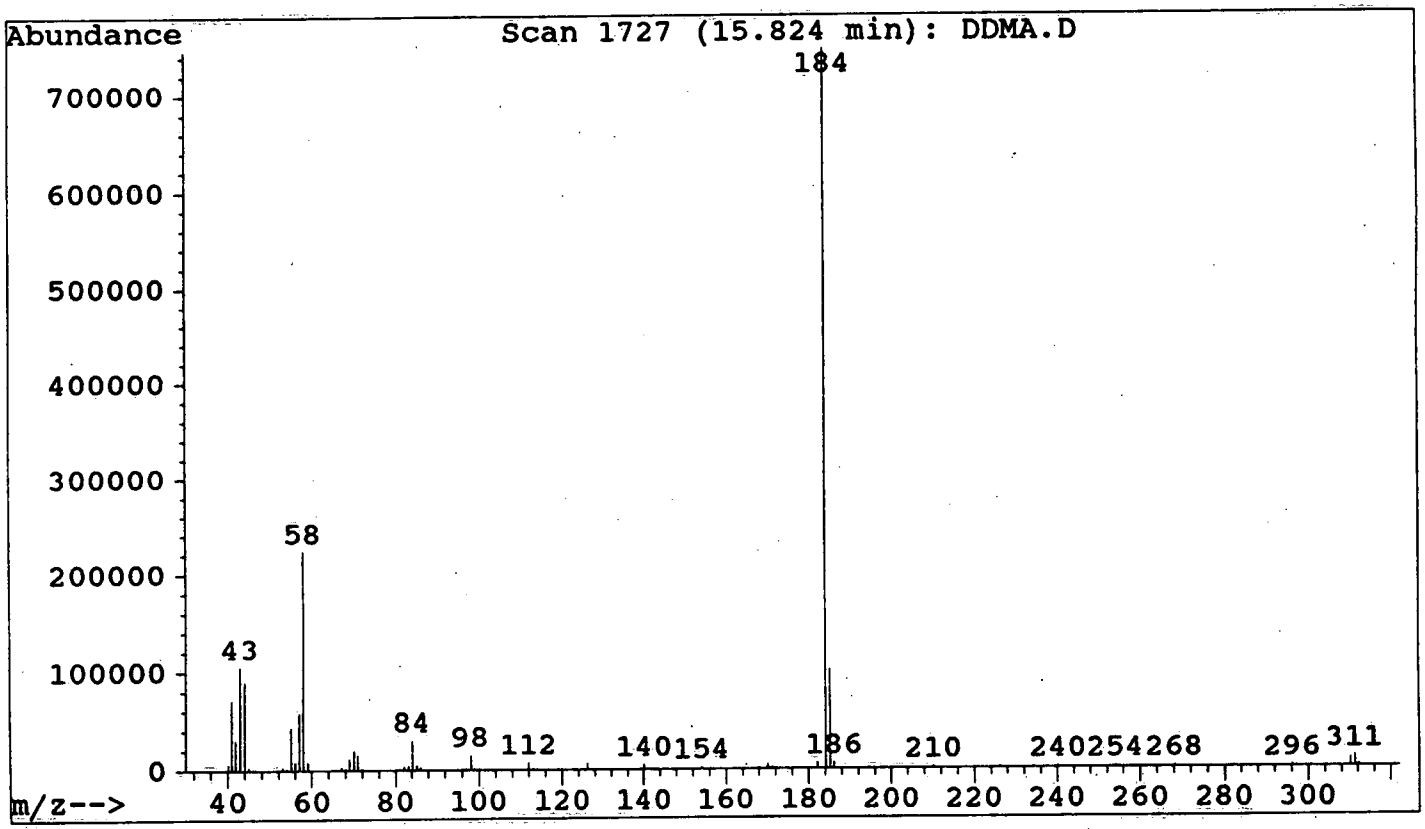
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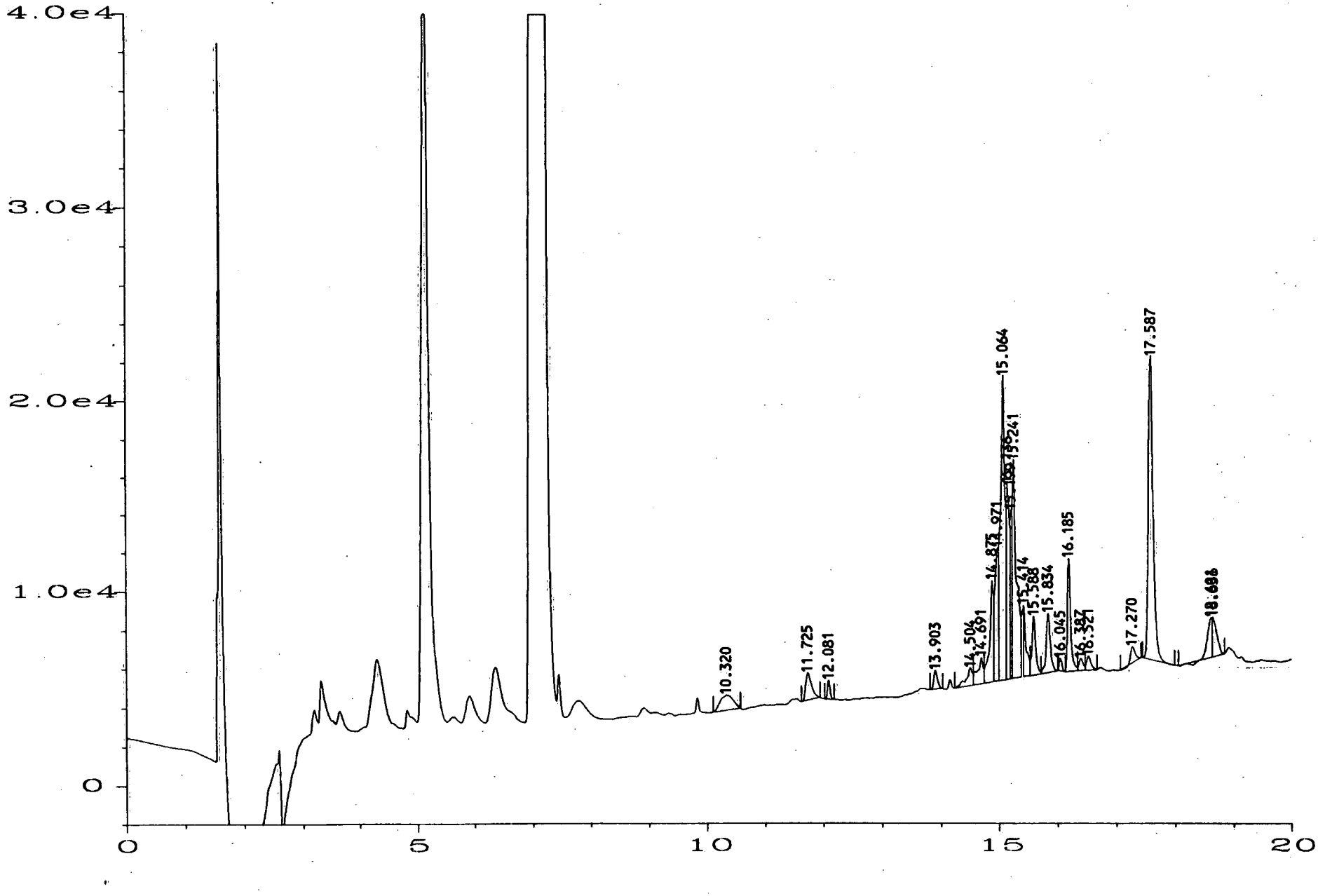
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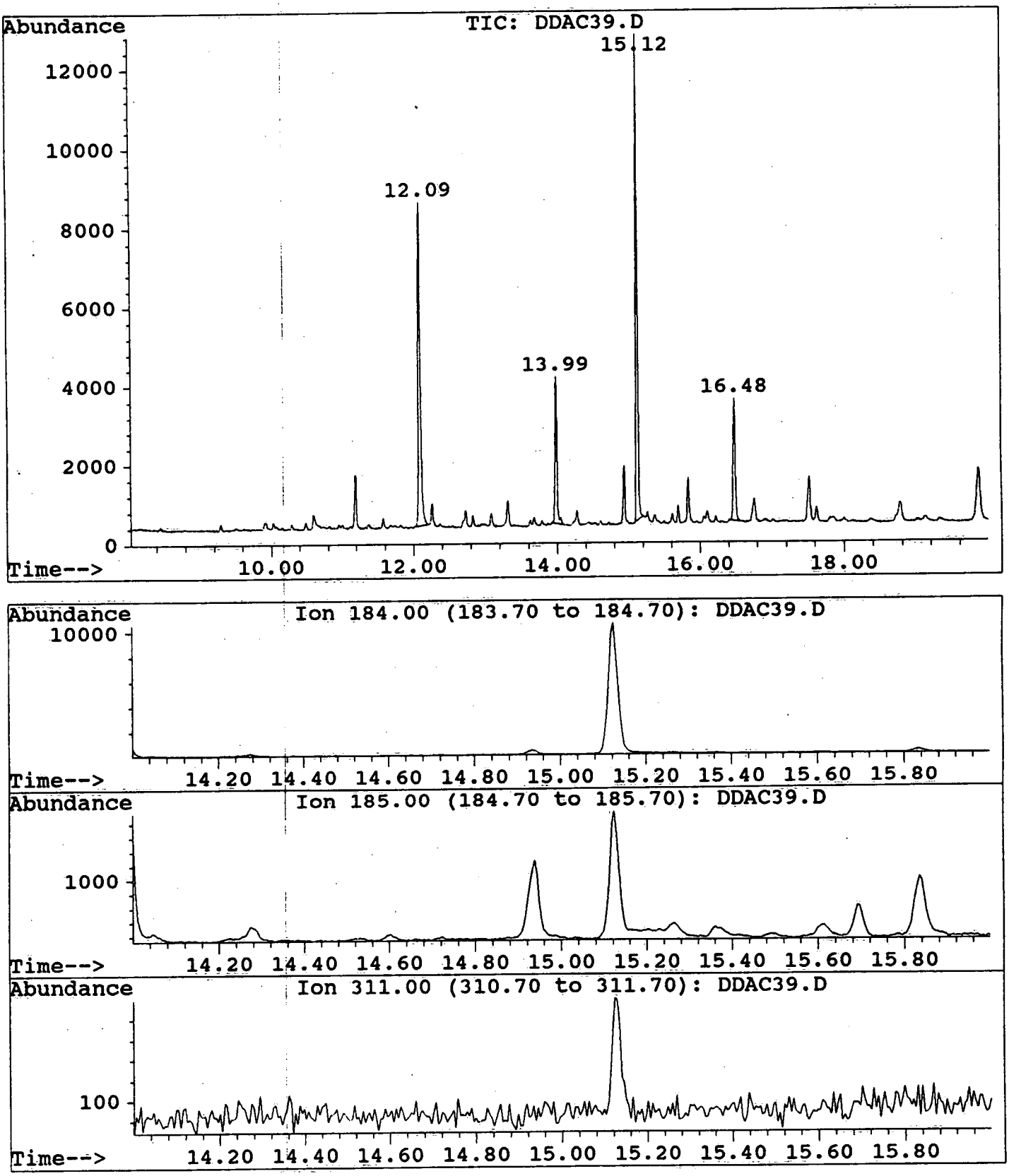
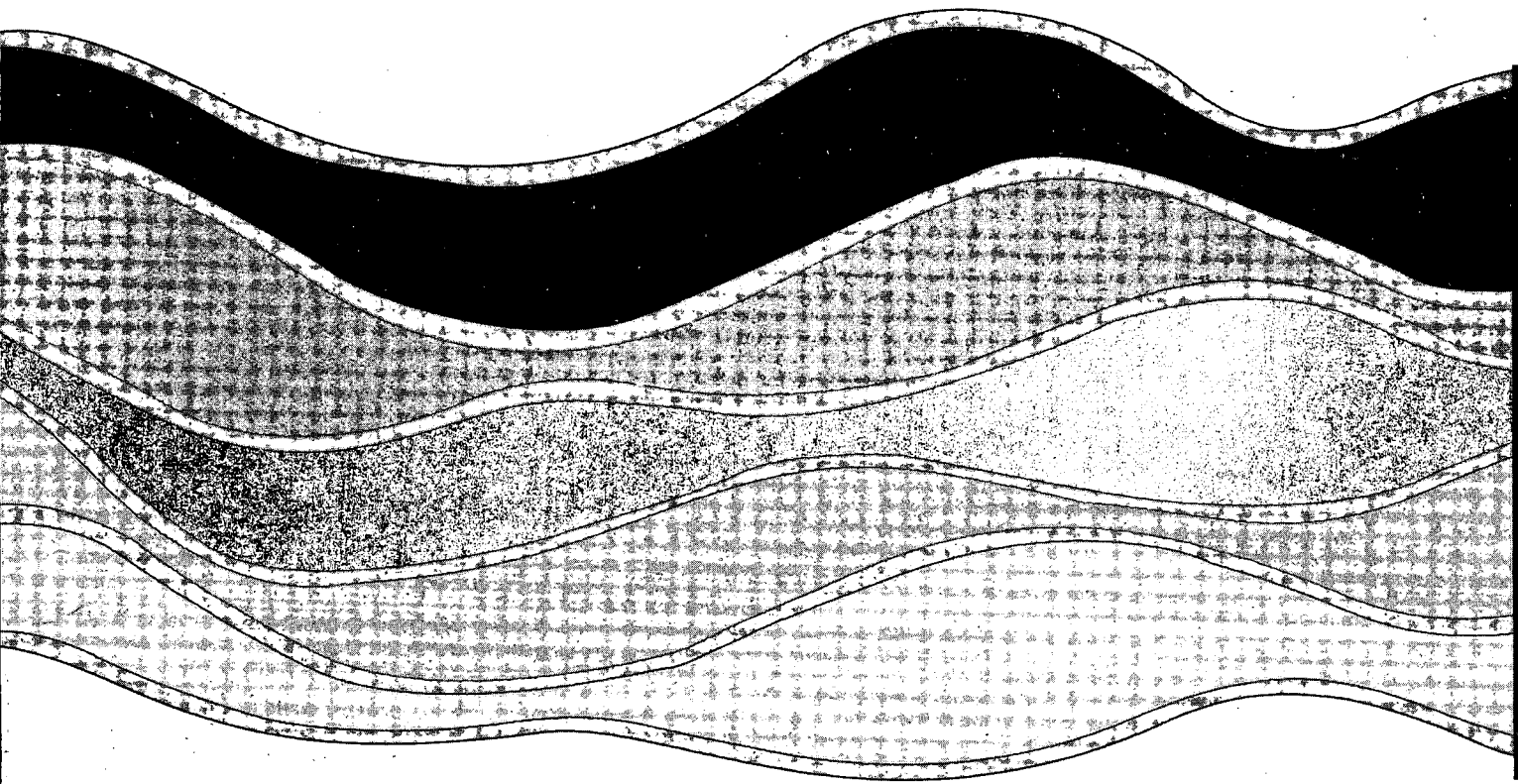
15.834
16.045
16.185
16.387
16.521
17.270
17.587
18.698

Figure 3

Figure 4


Abundance
TIC: DDAC39.D
15.12
12000
10000
12.09
8000
6000
13.99
4000
16.48
2000
0
Time-->
10.00
12.00
14.00
16.00
18.00
Abundance
Ion 184.00 (183.70 to 184.70): DDAC39.D
10000
Time-->
14.20 14.40 14.60 14.80 15.00 15.20 15.40 15.60 15.80
Abundance
Ion 185.00 (184.70 to 185.70): DDAC39.D
1000
Time-->
14.20 14.40 14.60 14.80 15.00 15.20 15.40 15.60 15.80
Abundance
Ion 311.00 (310.70 to 311.70): DDAC39.D
100
Time-->
14.20 14.40 14.60 14.80 15.00 15.20 15.40 15.60 15.80



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