A mild extraction method for element speciation analysis from feather matrices
Determination of organotin species from Surf Scoter feather

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Management Perspective

Speciation analysis of organometallic compounds in biological samples has been a challenging problem for analytical chemists. The major difficulties are the dissolution of samples without destruction of the chemical structure of the analytes. Fifty-two Surf Scoter feather and liver samples from the west coast of Canada were collected by the Canadian Wildlife Service for the determination of the very toxic butyltin compounds (mono-, di-, and tributyltin) with a view to investigating the occurrence and contamination of butyltin in this marine duck. The relationship of total butyltin concentrations in feather and liver tissue can be established to assess the possibility of using feather as an indicator for non-killing monitoring on the contamination of butyltin compounds in water birds. A special extraction method was developed for the butyltin species in duck feather. Experimental results indicated that butyltin compounds could go through the feather digestion procedure without decomposition and the recoveries were 96±3, 95±3, 86±6 and 96±4 for mono-, di-, tributyltin and tripentyltin. This extraction method can also be applied for the other acidic and thermally labile compounds, particularly for element speciation in feather or hair matices.

Sommaire à l'intention de la direction

L'analyse des composés organométalliques des spécimens biologiques pose des problèmes épineux aux chimistes. La principale difficulté est de dissoudre les tissus sans détruire la structure des composés recherchés. Le Service canadien de la faune a prélevé 52 échantillons de plumes et de foie de macreuse à front blanc sur la côte ouest canadienne pour y rechercher les composés très toxiques du butylétain (monobutylétain, dibutylétain et tributylétain) afin d'évaluer la contamination de cet oiseau marin. On a étudié la relation caractérisant les concentrations totales de composés du butylétain dans les plumes et le foie en vue de déterminer s'il est possible d'utiliser les plumes comme indicateur de la contamination des oiseaux aquatiques par le butylétain, ce qui permettrait de surveiller cette contamination sans sacrifier d'oiseaux. Une méthode spéciale a été mise au point pour extraire les composés du butylétain des plumes d'oiseaux aquatiques. D'après les résultats des expériences, les composés du butylétain peuvent subir le procédé de digestion des plumes sans se décomposer (récupération de 96 ± 3 pour le monobutylétain, 95 ± 3 pour le dibutylétain, 86 ± 6 pour le tributylétain et 96 ± 4 pour le tripentylétain). Cette méthode peut servir à extraire d'autres composés acides et thermolabiles, plus particulièrement pour l'analyse chimique des plumes et des poils.

Abstract

Fifty-two Surf Scoter feather and liver samples from the west coast of Canada were collected by the Canadian Wildlife Service for the determination of butyltin compounds (mono-, di-, and tributyltin) with a view to investigating the occurrence and contamination of butyltin in this marine duck. The relationship of total butyltin concentrations in feather and liver tissue can be established to assess the possibility of using feather as an indicator for non-killing monitoring on the contamination of butyltin compounds in water birds. A special extraction method was developed for the butyltin species in duck feather. Experimental results indicated that butyltin compounds could go through the feather digestion procedure without decomposition and the recoveries were 96±3, 95±3, 86±6 and 96±4 for mono-, di-, tributyltin and tripentyltin. This extraction method can also be applied for the other acidic and thermally labile compounds, particularly for element speciation in feather or hair matices.

Keywords: feather, digestion, butyltin compounds, duck

Résumé

Le Service canadien de la faune a prélevé 52 échantillons de plumes et de foie de macreuse à front blanc sur la côte ouest canadienne pour y rechercher des composés du butylétain (monobutylétain, dibutylétain et tributylétain) afin d'évaluer la contamination de cet oiseau marin. On a étudié la relation caractérisant les concentrations totales de composés du butylétain dans les plumes et le foie en vue de déterminer s'il est possible d'utiliser les plumes comme indicateur de la contamination des oiseaux aquatiques par le butylétain, ce qui permettrait de surveiller cette contamination sans sacrifier d'oiseaux. Une méthode spéciale a été mise au point pour extraire les composés du butylétain des plumes d'oiseaux aquatiques. D'après les résultats des expériences, les composés du butylétain peuvent subir le procédé de digestion des plumes sans se décomposer (récupération de 96 ± 3 pour le monobutylétain, 95 ± 3 pour le dibutylétain, 86 ± 6 pour le tributylétain et 96 ± 4 pour le tripentylétain). Cette méthode peut servir à extraire d'autres composés acides et thermolabiles, plus particulièrement pour l'analyse chimique des plumes et des poils.

Mots-clés

Plumes, digestion, composés du butylétain, oiseaux aquatiques

INTRODUCTION

The antifouling use of tributyltin (TBT) began in the 1960s. Since then TBT has resulted in deleterious effects on a variety of non-target organisms. The occurrence of extremely toxic TBT compound in the aquatic environment[1,2,3] and aquatic organisms [4,5] has been documented in the literature. Recently, the occurrence of tributyltin and its degradation products has been reported in water birds [6-9]. It was suggested that butyltin compounds could be accumulated in liver and kidney of the water birds.

Surf Scoter is a kind of marine duck and can be used to assess the TBT contamination in aquatic environment and bioaccumulation in marine birds in the west coast of Canada. With the determination of TBT in duck organs and feather, the relationship of total butyltin concentrations in feather and liver tissue can be established to assess the possibility of using feather as an indicator for non-killing monitoring on the contamination of butyltin compounds in water birds.

Difficulties in speciation analysis of biological samples include dissolution of samples without destruction of the chemical structures of the analytes, and the isolation of the analytes from the complex sample matrices for analysis. The conventional acid digestion or ashing techniques with oxidizing acids are not suitable for butyltin compounds. In this study, a mild extraction method was developed for determination of organotin compounds in duck feather. To our knowledge, this is the first report on the digestion of a feather matrix with TMAH (tetramethylammnium hydroxide) compounds.

EXPERIMENTAL

Reagent and instruments

The organotin compounds and special reagents were obtained from either Alfa AESAR (Ward Hill, MA) or Aldrich (Milwaukee, WI). Other solvents, acids and common laboratory reagents were of analytical grade. Distilled water further purified by the Milli-Q system (Millipore, USA) was used throughout the experiments. Individual stock solutions of organotin compounds (1000μg mL^{-1} as Sn) were prepared by dissolving the equivalent amounts of organotin in methanol or toluene. Speciation analysis of the butyltin compounds was carried out by the GC-AED or GC-FPD techniques. GC-MSD was used to confirm these compounds from environmental samples. The operating conditions for GC-AED, GC-FPD and GC-MSD were reported before[10-11] and listed in table 1. The limits of detection and quantitation for each butyltin species in feather were 2.0 and 10.0 ng Sn/g for 0.5g sample by means of GC-AED system.

Table 1. Operating parameters of GC-AED, GC-MSD and GC-FPD

GC-AED	
Injection port	Splitless
Injection port temperature	250°C
Injection volume	1 μL
Column	SPB-1, 30 m x 0.53 mm I.D.
Column head pressure	100 kPa
Temperature program	60°C for 2 min, then 20°C/min to 250°C with 3.5 min final hold
Transfer line	SPB-1
Transfer line temperature	270°C
Cavity temperature	270°C
Solvent vent time	1.5 min
Spectrometer purge gas	N_2 at 2 L/min
Helium makeup gas flow rate	240 mL/min
Sn wavelength	271 nm
H_2 pressure	414 kPa

O_2 pressure	138 kPa
GC-MSD	
Splitless injection	Purge time 1.0 min
Injector temperature	250°C
Injection volume	1 µL
Column	DB5, 30m x 0.25 mm I.D.
Carrier gas	He
Temperature program	50°C for 1 min, then 20°C/min to 280°C, with 2.5 min final hold
Detector temperature	280°C
Ionization potential	70 eV
Source temperature	190°C
Species (ethylated derivatives)	Ion Monitored
MBT	121, 149, 179
DBT	121, 149, 179
TBT	121, 149, 177
MPT	197, 255, 121
DPT	120, 197
TPT	120, 197
GC-FPD	
Splitless injection	Purge time 1.0 min
Injector temperature	250°C
Injection volume	1 µL
Column	DB5, 30m x 0.25 mm I.D.
Carrier gas	He
Temperature program	50°C for 1 min, then 20°C/min to 280°C, with 2.5 min final hold
Detector temperature	200°C
Combustion gases	H_2 and air, each at 100 mL/min

Sample preparation

For organotin speciation analysis from feather matrices, the conventional acid digestion or ashing techniques with oxidizing acids are not suitable. This problem can be overcome by the use of tetramethylammonium hydroxide (TMAH), which digests the sample and liberates the analytes of interest.

Feather samples (0.1-0.5g), spiked with tripentyltin (TPeT) as an internal standard, were digested in 20 mL of 20% aqueous solution of TMAH in a 50-mL Erlenmeyer flask at

65°C on a hot plate for 90 min with occasional shaking. After the addition of 20 mL of acetic acid, 8 g of NaCl and 4 mL of 0.2 % tropolone/toluene solution, the mixture was magnetically stirred for 20 min, then 2 mL of toluene was removed and dried using a stream of nitrogen. The volume was brought back to 1 mL with hexane and allowed to react with 0.3 mL of ethylmagnesium bromide (1.0M in THF) for 3 min. After the destruction of the excess ethylmagnesium bromide by 2 mL of 1N H_2SO_4, the organic layer was quantitatively removed and cleaned by silica gel in a micro column using a Pasteur pipette (packed with 5 cm of silica gel, topped with 1 cm anhydrous Na_2SO_4) and eluted with 5 mL of hexane. After reduction of the eluate volume to 1 mL by nitrogen, 1 μL of the eluate was injected into the GC systems for analysis.

RESULTS AND DISCUSSION

The experiment of recoveries was performed by spiking 200 μL of a mixed MBT, DBT, TBT, MPT, DPT, TPT and TPeT standard solution (1 μg Sn/mL) to 0.5 g of feather sample. The sample was dried in the air for 1 hour and went through the whole extraction procedure as mentioned above. The recoveries were evaluated by comparing the peak areas to those of the corresponding butyltin compounds of a mixed standard solution directly derivatized with ethylmagnesium bromide without the sample and without going through the extraction and the clean-up procedures. The recoveries for individual organotin compounds are given in Table 2.

Table 2. Recoveries of butyltin and phenyltin species from spiked feather samples

MBT	DBT	TBT	MPT	DPT	TPT	TPeT
96±3	95±3	86±6	139±5	132±2	49±6	96±4

In spite of the multiple steps involved in sample dissolution and clean-up procedures, the recovery rates for individual butyltin compound are satisfactory. Because large amount of MPT and DPT , the degradation products of TPT, were observed from the recovery tests, the decomposition of phenyltin species was believed to occur at acidic condition required for the tropolone extraction. The decomposition of phenyltin species in acidic medium has been confirmed by other studies.[11-12]

In conclusion, analysis of feather samples normally requires a digestion step for breaking down the sample to release the analytes of interest prior to any analytical procedures. The common digestion procedures involving the use of strong acids or oxidizing agents are not suitable for element speciation analysis. The present developed technique has been successfully used for the digestion of feather samples without altering the chemical forms (speciation) of the analytes. This method can also be applied for the determination of other acidic and thermally labile compounds in feather or hair matices.

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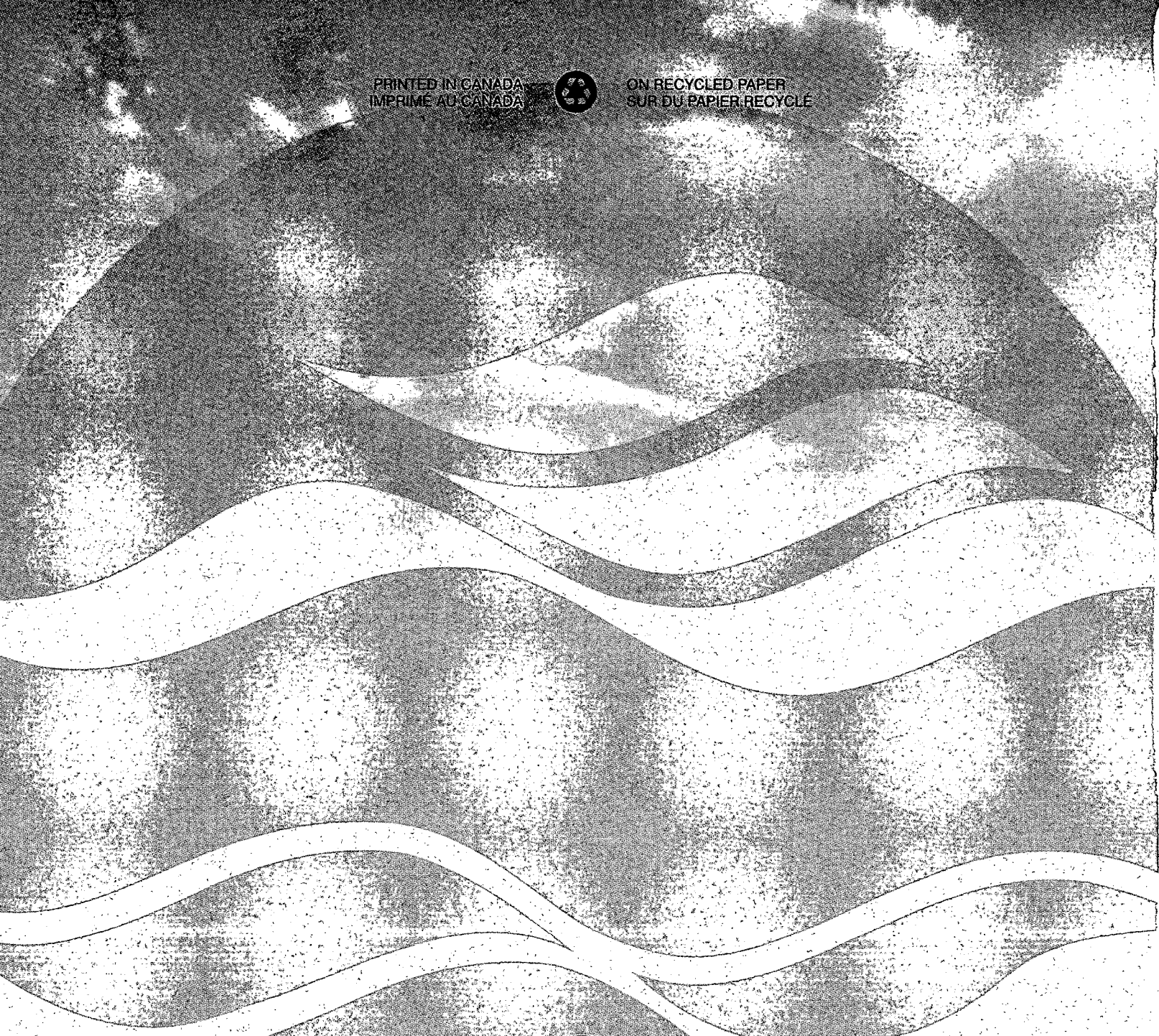

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