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Thallium, Uranium, and $^{235}U/^{238}U$ Ratios in the Digestive Gland of American Lobster (*Homarus americanus*) from an Industrialized Harbor

C. L. Chou, J. F. Uthe

Marine Chemistry Division, Physical and Chemical Sciences Branch, Scotia-Fundy Region, Department of Fisheries and Oceans, P.O. Box 550, Halifax, Nova Scotia, B3J 2S7, Canada

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Many earlier studies have concentrated on common transition elements with known biological functions and toxicological significance, e.g. cadmium, lead, copper, zinc (Vernberg et al. 1985), but fewer on others such as thallium (Tl). Zitko (1975) reviewed the toxicity of Tl as an environmental contaminant resulting from mines; ore-processing plants, especially the processing of sulfide ores (Smith and Carson 1977); and coal-burning power stations. Flegal et al. (1986) reviewed the available information on Tl concentrations in marine species, ranging 100-140 $ng \cdot g^{-1}$ wet wt. for Teleosti and <500 $ng \cdot g^{-1}$ for Mollusca. Hsieh et al. (1982) reported that "fresh fish" contained 2.6 $\mu g\ Tl \cdot g^{-1}$ wet wt. The average daily human intake of Tl is estimated to be ca. 2 µg (Smith and Carson 1977).

Tl measurement in environmental samples has been reviewed by Smith and Carson (1977). Graphite furnace atomic absorption spectrophotometry has the necessary sensitivity, but suffers from interference and loss (Tl nitrates may be lost during the ashing step). Inductively coupled plasma emission spectrometry (ICP-AES) suffers from poor sensitivity for Tl.

Uranium (U) has been studied as a radionuclide of concern in food and the environment (Berlin and Rudell 1979). Foodstuffs contain 10-100 $ng\ U \cdot g^{-1}$, with vegetables and cereals contributing most heavily to the daily intake of ca. 1.5 µg U (Welford and Baird 1967). Between 10-30% of ingested U is absorbed, with most being stored in bone (Berlin and Rudell 1979). Rainbow trout (*Onchorynchus mykiss*) and longnose sucker (*Catostomus catostomus*) from a lake with naturally high radioactivity contained < 5 $ng\ U \cdot g^{-1}$ in the flesh (Mahon 1982). Trout bone contained 40 $ng\ U \cdot g^{-1}$. Higher tissue U concentrations occurred in fish from areas receiving U mining wastes (Swanson 1983). Bioconcentration factors for bone and flesh were estimated to be low, 118 and 14.7, respectively (Mahon 1982).

Inductively coupled plasma-mass spectrometry (ICP-MS) has been used for measurement of the U series of elements in environmental samples, e.g., vegetation, soil, dust, and air (Boomer and Powell 1987). One advantage of using ICP-MS is its specificity and lower detection limits compared to optical methods. ICP-AES has been used

Correspondence to: C. L. Chou

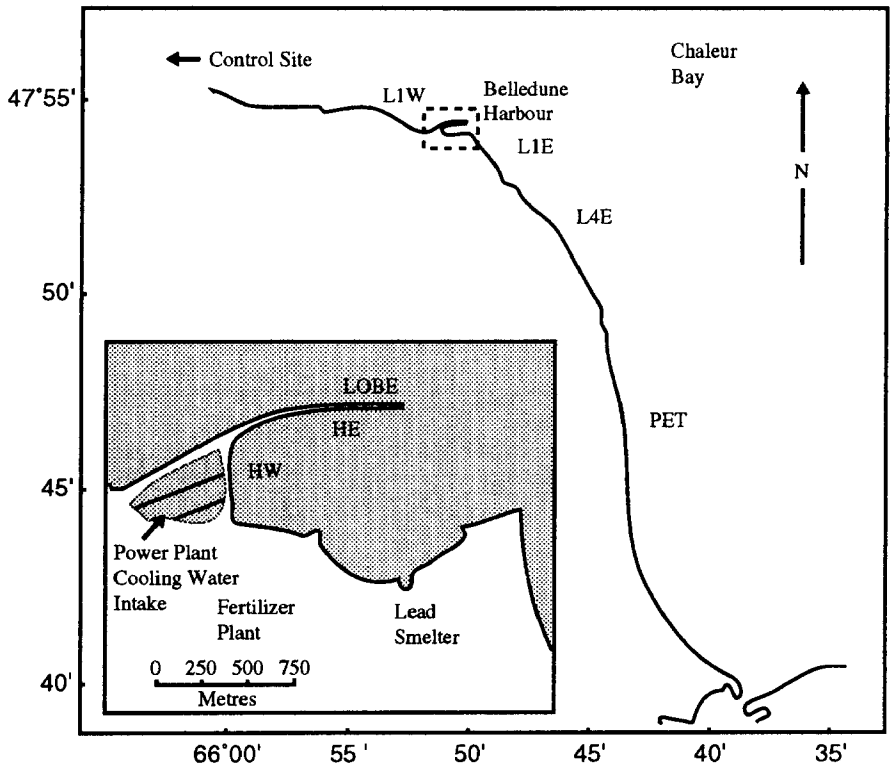

Figure 1. Lobster capture sites in the area of Belledune Harbor, New Brunswick, Canada.

for U analysis (Huff and Bowers 1990). However, it is subject to spectral interferences and has relatively high detection limits. Other common techniques, e.g., α-radiometry, spectrometry, fluorometry, are slow, tedious (i.e., the addition of tracers, separation procedures such as chelation, electroplating, or ion-exchange), and subject to interferences.

This paper describes the ICP-MS determination of Tl and U in digestive gland tissue from lobsters captured in the vicinity of Belledune Harbor, New Brunswick, Canada. The harbor is the site of a lead smelter, a fertilizer plant, and a coal-fired power station (the latter due to enter production in late 1993) and thus has the potential of adding significant amounts of Tl to the local marine environment (Zitko 1975). Tl was stated by Zitko (1975) to be slightly more acutely toxic to mammals than mercury. Reports on the chronic toxicity of Tl to marine organisms were not found. The accumulation of Tl from water by marine shellfish is low (Zitko and Carson 1975), at least for bivalves, and the accumulated Tl is

Table 1. Instrumental parameters of the ELAN 5000 ICP-MS.

	RF Power	1000 watts
	Plasma gas flow	15 $L \cdot min^{-1}$
	Auxiliary gas flow	0.8 $L \cdot min^{-1}$
	Nebulizer gas flow	0.9 $L \cdot min^{-1}$
	Sampler	Nickel
	Skimmer	Nickel
	Operating Conditions	
	Tl and U	^{235}U and ^{238}U
Dwell time	600 ms.	300 ms.
Replicate time	7200 ms.	36000 ms.
Reading	12 sweeps	12 sweeps
Replicate	3 readings	10 readings
Scanning	Peak hop	Peak hop
Time factor		12 for ^{235}U
Resolution	Normal	Normal

eliminated in a number of days when the animals are transferred to clean water. Bioconcentration factors for U in finfish ranged from 0.4-17 for larger species (Swanson 1983). However, because of the high concentrations of various trace elements in lobster digestive gland (Chou and Uthe 1993), its desirability as a foodstuff, and its relatively large size (approximately 20% of the edible tissue yield [Stewart et al. 1967]), we have investigated Tl and U concentrations and $^{235}U/^{238}U$ ratios in it.

MATERIALS AND METHODS

Lobster capture sites are shown in Figure 1. The control site was located on the seaward side of Heron Island in Chaleur Bay. Animals (15-20 per site) were captured by local fishermen using conventional trapping methods in May, 1992. They were transported live to the laboratory where each intact digestive gland was rapidly removed and homogenized by hand-kneading in Whirl-Pak bag. One pooled sample was prepared per site using 3 g portions. Three subsamples (0.800-1.200 g) of each pool were digested in calibrated 50-mL Folin-Wu tubes (BDH boiling chips) with 5 mL conc. HNO_3. The tubes were heated gently until frothing ceased, then gently refluxed on microKjeldahl heating racks for 6 hr. After cooling, each digest was made up to 25 mL with quartz-distilled H_2O, covered with Parafilm, and left at room temperature for 2 days to allow the residual fat to clump as a floating mass. A portion of the clear aqueous phase was taken and further diluted (1:3) with H_2O for analysis (an overall dilution of 1:75).

A Perkin-Elmer SCIEX ELAN 5000 ICP-MS was used throughout. The system is equipped with a four-channel mass flow controller to

Table 2. Accuracy and precision in the determination of thallium and uranium ($ng \cdot g^{-1}$ wet wt.) in lobster digestive gland and NIST oyster reference material by nitric acid dissolution and ICP-MS using external standardization and the method of standard additions. (Standard deviation is shown, N = 3)

	Thallium		Uranium	
Sample Site	External Standard	Method of Standard Additions	External Standard	Method of Standard Additions
Control	8.89±0.14	9.05±0.26	10.34±0.26	10.95±0.52
LOBE	45.62±0.02	44.86±0.92	95.03±1.07	93.33±2.17
HW	193.5±3.0	199.0±3.2	45.07±5.08	44.66±1.68
NIST-SRM Oyster	not analyzed	not analyzed	99.88±3.65	106.3±4.2
Certified Value	uncertified	uncertified	116±6	116±6

stabilize all plasma gas flows. A standard corrosion-resistant spray chamber (Ryton), a cross-flow nebulizer, and a Perkin-Elmer Model AS 90 random access autosampler were used. Table 1 lists instrumental parameters. Lower limits of detection were 6, 4.5, and 7 $pg \cdot mL^{-1}$ for Tl, ^{235}U, and ^{238}U, respectively, based on 3 σ of blank intensity counts. This corresponds to concentrations of 0.45 ng $Tl \cdot g^{-1}$, 3.37 ng $^{235}U \cdot g^{-1}$, and 0.53 ng $^{238}U \cdot g^{-1}$ for 1 gram wet tissue.

A series of standard solutions, containing 0.5, 1.0, and 2.0 $ng \cdot mL^{-1}$ Tl and U, were prepared in 1% HNO_3 and used as external calibration standards. Thorium (10 $ng \cdot mL^{-1}$) was added on-line to correct for drift of the ICP-MS. Analyses also employed the method of standard additions (two additions, three-point simple linear extrapolation to yield the intercept for correcting for matrix interferences). The HNO_3 blank value was negligible (ca. 15 $counts \cdot sec^{-1}$).

The standard solutions were prepared from single element (1.000 $mg \cdot mL^{-1}$) standards (SPEX Industries, NJ). A standard solution containing 1.0 ng $U \cdot mL^{-1}$ and a $^{235}U/^{238}U$ ratio of 0.0072 was used to calibrate the $^{235}U/^{238}U$ ratio in the samples. Calibration curves were calculated from the intensity ratios of the thorium internal standard and the analytes. The $^{235}U/^{238}U$ isotope ratios were calculated for each sample and our U standard.

RESULTS AND DISCUSSION

No differences were found in Tl and U concentrations in selected lobster digestive gland pooled samples as determined by external standardization and the method of standard additions (Table 2). The samples were selected to span the concentration ranges of both

Table 3. Thallium and Uranium Concentrations ($ng \cdot g^{-1}$ wet wt.) and $^{235}U/^{238}U$ Ratios in Lobster Digestive Gland from Belledune Harbor, New Brunswick, Canada. (Standard deviation is shown, N = 3)

Sample Site	Thallium	Uranium	$^{235}U/^{238}U$ Ratio
Control	8.89±0.14	10.34±0.26	0.0082±0.0003
L1W	38.60±0.77	19.52±0.54	0.0081±0.0002
LOBE	45.62±0.02	95.03±1.07	0.0078±0.0001
HW	193.5±3.0	45.07±5.08	0.0078±0.0001
HE	170.3±1.2	44.61±1.25	0.0078±0.0001
L1E	155.4±0.7	20.95±0.84	0.0082±0.0001
L4E	48.25±0.52	17.13±0.30	0.0083±0.0000
PET	31.22±1.06	14.52±0.53	0.0084±0.0001
U Standard			0.0073±0.0001

elements. The excellent agreement between standard addition and external calibration procedures suggests that diluted HNO_3 digests of lobster digestive gland contained no material with significant matrix effects on Tl and U measurement. However, only the method of standard additions gave the certified U concentration with the NIST oyster tissue, No. 1566 (Table 2). External standardization gave low values (Table 2), suggesting that the nitric acid procedure is not suitable for oyster tissue when external standardization is used. Dry oyster tissue (ca. 0.25 g, equivalent to 1-1.5 g wet tissue) had been digested.

Tl concentrations were elevated (Table 3) compared to the control in digestive glands from lobsters captured within Belledune Harbor and at the L1E site (the discharge area of treated aqueous effluent from the lead smelter). The source of Tl within Belledune Harbor is obscure. The smelter has not discharged effluent into the harbor since late 1980, although a break in an underground pipe prior to the 1986 lobster survey (Chou and Uthe 1993) at the smelter led to substantial and continuing recontamination of harbor lobsters thereafter. Also the exposure of bedrock during harbor dredging and modification for a coal-fired power plant in 1990-1991 may have released Tl. Tl concentrations at sites near the fertilizer plant discharge (LOBE site) were also elevated compared to controls, but less than observed in the harbor. The above suggests that both the fertilizer plant and the lead smelter are sources of Tl. Power plant operation can be expected to increase Tl input to the local environment (Smith and Carson 1977; Zitko 1975).

In contrast to the distribution of Tl in lobster digestive glands, U concentrations were highest near the fertilizer plant outfall (Table 3; LOBE site). U concentrations in harbor lobster digestive glands

were about one-half LOBE concentrations and still lower at the L1E site, where treated smelter effluent is discharged. $^{235}U/^{238}U$ ratios in uncontaminated lobsters from Chaleur Bay show enrichment compared to the geological mean of 0.711% ^{235}U by weight (Weast 1975) and are inversely related to U concentrations, suggesting the anthropogenic U had a $^{235}U/^{238}U$ ratio nearer the geological mean.

In conclusion, incomplete sample dissolution with nitric acid is acceptable for the determination of Tl and U in lobster digestive gland samples by ICP-MS. The method is straightforward, with no need for further chemical treatment prior to analysis by ICP-MS. Lobsters from Belledune Harbor and its immediate environs contain elevated Tl and U concentrations, the significance of which should be assessed from the perspective of protection of seafood consumers.

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