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Determination of Vanadium and Nickel in Marine Samples by Flameless and Flame Atomic Absorption Spectrophotometry

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In recent years, oil contamination in marine environments by tanker collisions and accidental discharges from petroleum industries have occurred often. Therefore, oil contamination has become a serious problem not only with the coastal fishes and the cultural fisheries, but also for man, because various petroleum components easily transfer to man via fishes and shellfishes. For the fingerprint of oil contamination, organic compounds, such as *n*-paraffins, polyaromatic hydrocarbons and sulfur compounds are used (NAKAMURA and KASHIMOTO 1978).

With respect to heavy metals, vanadium and nickel are main component in crude oil. However, there are few reports on heavy metals in marine products when compared with heavy metals in crude oil. Therefore, vanadium and nickel were selected as an indicator for the study of the pollution of the marine environment by petroleum.

Colorimetric methods are predominantly used for the analysis of vanadium, however, these methods do not give satisfactory sensitivity (COOPER and WINTER 1949, RILEY and TAYLER 1968, YOTSUYANAGI *et al.* 1969, YAMANE *et al.* 1974).

On the other hand, with respect to analytical method for vanadium, atomic absorption spectrophotometry (AAS) in a nitrous oxide-acetylene flame is mainly used; this is hazardous and gives low sensitivity (SACHDEV *et al.* 1967, CHAU and LUM-CHUE-CHAN 1970). OMANG (1971) reported the analysis of vanadium in mineral oil by use of the flameless AAS with better sensitivity. However, there are few reports on analyses of foods.

In this paper the authors determined vanadium in foods, especially in fish and shellfishes by the use of flameless AAS. Analysis of nickel was determined by flame AAS in a air-acetylene flame.

EXPERIMENTAL

Reagents

All of the reagents used were analytical reagent grade from Wako Pure Chemical Ind., Ltd.

Preparation of vanadium standard solution: 0.230 g of ammonium metavanadate were dissolved in 100 mL of 0.5N HCl to yield 1000 μg/mL of vanadium.

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Preparation of nickel standard solution: 0.220 g of nickel chloride were dissolved in 100 mL of 0.5N HCl to yield 1000 μg /mL of nickel.

Apparatus

Atomic absorption spectrophotometer: Varian Techtron AA-5

Flameless atomic absorption spectrophotometer: Varian Techtron Model 63 carbon rod atomizer

Low temperature asher: International Plasma Corporation-1101 B Type

Freeze dry apparatus: LAB CON CO Model 75010

Spectral source: Varian Techtron Hollow Cathode V and Ni Lamp

L_{233}-IQD type of Hamamatsu Television Ltd. was used for background correction.

Vanadium Instrument Condition

A Varian Techtron, Model AA-5 atomic absorption spectrophotometer with a Varian Techtron Model 63 carbon rod atomizer was used. Samples were atomized with ramp mode on operation. The most suitable measurement conditions were as follows:

a) Carbon rod atomizer

Dry-voltage setting; 5 V, drying time; 40 s, Ash-voltage setting; 4 V, ashing time; 20 s, ramp atomize cut-off voltage; 9.5 and ramp rate; 4, N_2 flow; 4.5 L/min, cooling water; 1.5 L/min

b) Instrument parameters

Wavelength; 318.4 nm, slit width; 100 μm, lamp current; 5mA

An Eppendorf microlitre pipette (5 μL) was used for measurement.

Nickel Instrument Condition

The most suitable measurement conditions were as follows:

Sample 10 g
↓
Freeze-drying for 24 h
↓
Ashing by low temperature asher
↓
Dissolution of the ash with 5 mL of dilute HCl
↓
Evaporation
↓
Dissolution of the residue with 10 mL of 0.5N-HCl
↙ ↘
Flameless AAS (V) Flame AAS (Ni)

Scheme 1. Analytical procedure for Vanadium and Nickel in marine samples by AAS.

Wavelength; 232.0 nm, slit width; 50 µm, lamp current; 5 mA, flame; air-acetylene

Material and Procedure

Shellfishes used were on the market in Osaka. The samples analysed are described in Table 1. Other samples in Table 2 were collected directly from the coast.

As summarized in Scheme 1, samples were freeze-dried for 24 h. Freeze-dried samples were ashed by a low temperature asher using the oxygen plasma. Ash was dissolved in dilute HCl. The solution was evaporated on the steam bath. This residue was diluted with 0.5N HCl and filled up to 10 mL and assayed.

RESULTS AND DISCUSSION

The concentration of vanadium and nickel in the seven oyser samples (two samples: cultured, five samples: natural) were determined. The samples analyzed are described in Table 1. Vanadium in these oyster has a narrow range of values, while nickel values have a wider ones. Eight samples of cord shell were analyzed. Five samples were obtained at Shinji lake in Shimane prefecture. Vanadium in cord shell was of the same order as that in oyster. However nickel in cord shell was detected at the high level of 8.60 ppm in one sample out of three from Mie prefecture.

Vanadium in nine samples of short-neck clam was detected at the average level of 0.067 ppm, which is lower than those in oyster and cord shell. Nickel in scallop was detected at the high level of 8.90 ppm in one sample out of three from Aomori prefecture.

Muscle and viscera in top-shell were separatedly determined; concentrations of vanadium and nickel in viscera were higher than those in muscle. Vanadium in viscera of top-shell was detected at the high level of 7.40 ppm in one sample out of three from Ise in Mie prefecture.

Concentration of vanadium and nickel in shellfishes, a crustacean (*Tetraclita squamosa japonica*) and a tunicate (*Halocynthia roretzi*) analyzed are given in Table 2. These samples were collected directly from the coast, partly because they can be easily collected, and partly because they are suitable for the fingerprint of oil contamination on the proper locations. *Cellana stearnsii*, *Collisella herolidi* and *Tetraclita squamosa japonica* showed slightly high level of vanadium.

Fig. 1 shows flameless AAS spectrograms of *Tetraclita squamosa japonica* analyzed (upper) and standard vanadium (lower).

Ascidian (*Halocynthia roretzi*) has long been believed to high level of vanadium (WEBB 1956). However concentration in

TABLE 1

Concentration of Vanadium and Nickel in Shellfishes

Sample	Catching or landing region	Concentration(ppm, wet base)	
		Vanadium	Nickel
Oyster	Hiroshima	0.084	0.086
"	"	0.187	0.160
"	Osaka	0.134	0.270
"	"	0.097	0.144
"	"	0.101	0.156
"	"	0.172	0.370
"	Oita	0.174	0.110
Average:		0.135	0.185
Cord shell	Shimane	0.110	1.776
"	"	0.052	0.384
"	"	0.110	0.454
"	"	0.221	3.620
"	"	0.116	1.076
"	Mie (Ise)	0.270	8.600
"	" (")	0.134	1.356
"	" (")	0.119	1.200
Average:		0.145	2.308
Short-neck clam	Mie (Ise)	0.104	0.976
"	" (")	0.097	0.824
"	Mie (Matsuzaka)	0.121	1.304
"	" (")	0.048	1.484
"	" (")	0.025	1.600
"	Hyogo	0.038	0.738
"	"	0.050	0.620
"	"	0.036	0.780
"	Shizuoka	0.089	0.556
Average:		0.067	0.986
Scallop	Aomori	0.104	0.776
"	"	0.094	0.724
"	"	0.328	8.900
Average:		0.175	3.460
Top-shell	Mie (Toba)	0.228	0.304
"	Mie (Ise)	0.232	0.450
"	" (")	0.112	0.322
"	" (")	0.160	0.520
Average:		0.183	0.399
Top-shell(viscera)	Mie (Toba)	0.536	0.890
"	Mie (Ise)	7.400	1.530
"	" (")	2.200	0.762
"	" (")	0.720	0.738
Average:		2.714	0.980

TABLE 2

Concentration of Vanadium and Nickel in Shellfishes

Sample	Catching or landing region	Concentration(ppm, wet base)	
		Vanadium	Nickel
Cellana stearnsii	Osaka	0.496	0.570
〃	Wakayama	0.584	1.910
〃	Oita	0.243	0.320
Average:		0.441	0.933
Liolophura japonica	Osaka	0.136	0.831
〃	Wakayama	0.359	0.791
〃	Oita	0.072	0.318
Average:		0.189	0.646
Liolophura japonica (viscera)	Osaka	0.991	2.010
〃	Wakayama	1.363	1.697
〃	Oita	0.103	1.090
Average:		0.819	1.599
Collisella heroldi	Osaka	0.528	3.200
〃	〃	0.364	3.520
Average:		0.446	3.360
Tetraclita squamosa japonica	Osaka	0.208	0.378
〃	〃	0.521	0.475
Average:		0.364	0.426
Mytilus edulis	Osaka	0.213	1.212
〃	California	0.156	0.304
Average:		0.184	0.758
Halocynthia roretzi	———	0.120	0.130

ascidian (*Halocynthia roretzi*) was lower than those in other shellfishes. Nickel was generally higher than vanadium, which shows same tendency in crude oil.

Table 3 shows analytical results for vanadium and nickel in fishes. Vanadium was detected in barracuda, black rockfish, sand borer and pollack roe, however, which showed low concentration when compared with shellfishes. Nickel in these fishes were lower than those in shellfishes.

On the other hand, vanadium in crude oil is reported to be less than nickel (HITCHON *et al.* 1973). AS shown in Table 1 and Table 2, nickel in shellfishes was higher than vanadium, which showed the same tendency as in crude oil. Nevertheless nickel in some fishes was reverse to the contents in crude oil.

Therefore it is necessary to clarify if these heavy metals in marine products result from oil pollution or they are natural

Fig. 1. Spectrograms of *Tetralita squamosa japonica* (upper) and standard vanadium (1 ng; lower) by flameless atomic absorption spectrophotometry.

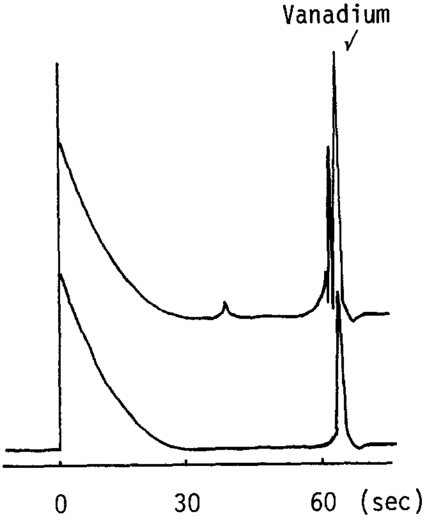

TABLE 3

Concentration of Vanadium and Nickel in Fishes

Sample	Catching or landing region	Concentration(ppm, wet base)	
		Vanadium	Nickel
Barracuda	Nagasaki	0.112	N D
"	Sanin	N D	0.034
Black rockfish	Sanin	0.075	N D
"	"	N D	0.142
"	"	"	0.034
"	"	"	0.062
"	Hokuriku	"	0.074
Sand borer	Australia	0.054	0.024
"	"	N D	0.060
"	Hyogo	"	0.092
"	Inland Sea of Seto	"	0.066
Pollack roe	Hokkaido	0.049	0.016
Mackerel	Saga	N D	N D
Flatfish	East China Sea	"	0.038
Squid	Hyogo	"	N D
Goosefish	Sanin	"	0.056
Salmon	Hokkai	"	0.022
Yellowtail (immature)	Shikoku	"	N D

Vanadium ; ND$<$ 0.020 ppm
Nickel ; ND$<$ 0.010 ppm

components in the tissues. Further investigations of annual variation of heavy metals in shellfishes and mutual relations between heavy metals and oil compounds in marine products are being studied.

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