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Determination of Total Organic Nitrogen and Organometallic Nickel in Oil, Sediments and Marine Products

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As a fingerprint of oil pollution in the sea environment, *n*-paraffins, olefins, polynuclear aromatic hydrocarbons, sulfur containing oil compounds, and heavy metals in crude oil are often selected and evaluated for the oil contamination of marine products and sediments(MALINS 1977).

Nitrogen containing oil compounds, however, are not documented for these analyses due to their trace existance in oil and the lack of more sensitive detection methods excepting high pressure liquid chromatography(HPLC) and gas liquid chromatography(GC) equipped with a nitrogen selective detector(HARTIGAN 1974, DONG 1977).

These nitrogen compounds consist of several categories of compounds, *i.e.*,basic and weak basic aromatic compounds such as quinoline, isoquinoline, carbazole, and porphirins. DRUSHELL(1976) reported a high sensitive method for determination of nitrogen containing oil compounds by a digital nitrogen analyzer using a chemiluminescence detection method.

In this paper, the authors determined total organic nitrogen contents in heavy oil, marine products and sediments by a digital nitrogen analyzer.

As an another parameter in heavy oil, IKEBE and TANAKA(1979) reported nickel and vanadium contents in marine products by flame and flameless atomic absorbtion spectrometry(AAS). These metals often exist in the forms of organometals such as petroporphirins(HAJIBRAHIM 1978). Therefore, organic Ni in oil and marine samples are also measured with respect to porphirins by flameless AAS. And the relation between nitrogen contents and organometallic nickel are evaluated.

EXPERIMENT

Reagent :

A, B-class heavy oil and C-class heavy oil(Koa Oil Co.) and C-class heavy oil(Mitsubishi Oil Co.) were obtained from Osaka Pollution Control Center and National Institute of Health, respectively. These oils dissolved in *n*-hexane, were used for the determination of nitrogen contents in oil and marine samples.

Preparation of nitrogen containing oil standard; Standard sample of nitrogen containing oil guaranteed by Japan Petroleum Institute (0.303 ± 0.003 wt%N) was purchased from Tokyo Kasei Co.,Ltd. and assayed in *n*-hexane solution.

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Preparation of Ni standard;0.220g of nickel chloride were dissolved in 100 mL of 0.5N HCl to yield 1000 μg/mL of nickel as reported by IKEBE and TANAKA(1979).

Analytical Instruments and Conditions :

Digital Nitrogen Analyzer: Antek 710 connected with Antek Pyrometer 711. Carrier gas; Ar 200 mL/min, Oxygen 500 mL/min, Temp.: Inlet 1000-1050°C, Center and Outlet 950-975°C.

Ni Instrument and Conditions: 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.

Conditions(1) Carbon Rod Atomizer, dry volt set.;5V, drying 40 sec, ash volt set.;4V, ashing time;20 sec., ramp atomize cut off volt;8.5V and ramp rate;4, Nitrogen gas flow;4.5 mL/min, cooling water;1.5 L/min.

(2) Instrument parameters: wavelength ;2320 nm, slit width;100 nm, Lamp current;5 mA.

Analytical Procedure of Samples;

Shellfishes analysed were from the market in Osaka. Sediments were collected in the Osaka Port. As previously reported(NAKAMURA and KASHIMOTO 1977, 1978), marine samples(fresh,wt 50g; sediments, dry matter 5g) were saponified with 2N KOH-ethanol (75 mL) for 1h. After saponification followed by the addition of the same portion of water, this phase was extracted with *n*-hexane(100 mL) three times. Hexane extracts were concentrated to 1-5 mL and separatedly assayed for the analyses of nitrogen and organometallic nickel contents.

RESULTS AND DISCUSSIONS

As shown in Table 1, total organic nitrogen contents in heavy oil were measured with the standard nitrogen calibration curve using standard oil by a digital nitrogen analyzer. From the experiment herein of a digital nitrogen analyzer using a chemiluminescence method, the minimun detecting limit of nitrogen in oil was 5 μgN. Total organic nitrogen in A-, B- and C-class heavy oil evaluated to be at the levels of 166-2448 ppm, which were at approximately one tenth levels of sulfur contents in these oils.

After saponification of heavy oil with alkaline ethanol, hexane extracts were measured for nitrogen and organometallic nickel,which implies the extractable metal with hexane. Through these procedure, porphirins were revealed to be fully recovered.

50-80% of total organic nitrogen in heavy oil were extracted by hexane after saponification.

By the experiment of nickel content in each sample, inorganic nickel chloride was obliged to be used due to the lack of organometallic nickel standard.

In case nitrogen contents vs organometallic nickel multiplied by 10^3 are calculated as Ni/N index, these indices are listed in Table 2. These values are evaluated to be identical each other at the levels of 16.3-25.7 despite of the difference of boiling fractions.

TABLE 1
Total Organic Nitrogen in Heavy Oil Determined by a Digital Nitrogen Analyzer

Oil*1	Total Organic Nitrogen(ppm*2)
A-class heavy oil	166
B-class heavy oil	1248
C-class heavy oil	2448

*1; Koa Oil Co.
*2; Average of three determinations using standard sample of nitrogen containing oil.

TABLE 2
Total Organic Nitrogen and Organometallic Nickel in the Hexane Extracts of Oil after Saponification and Ni/N Indices

Oil samples	ppm		Ni/N Indices*1
	Organic Nitrogen	Organometallic Nickel	
B-class heavy oil*2	760	19.5	25.7
C-class heavy oil*2	1916	46.5	24.2
C-class heavy oil*3	1196	19.5	16.3

*1; Organometallic Nickel/ Organic Nitrogen X 10^3
*2; Koa Oil Co.
*3; Mitsubishi Oil Co.

TABLE 3
Total Organic Nitrogen and Organometallic Nickel in the Hexane Extracts of Sediments from the Osaka Port and Ni/N Indices

Sediments samples	ppm(dry matter)		Ni/N Indices*1
	Organic Nitrogen	Organometallic Nickel	
No. 1	23.4	0.218	9.3
No. 2	7.89	0.149	18.8
No. 3	6.95	0.180	25.8

*1; Organometallic Nickel/ Organic Nitrogen X 10^3

On the other hand, total nitrogen and organometallic nickel of sediments collected from the Osaka Port are described in Table 3. Ni/N indices are listed in the same table.

Sample No. 1 is located just near the mouth of river, No. 2 is from the outer part of the Port, and No. 3 is from the middle point between No. 1 and No. 2. These distances are ca. 3.7 km far each other. Organic sulfur containing oil compounds were reported to be at 7.51 ppm(No.1), 0.673 ppm(No.2), and 0.812 ppm(No.3)(dry matter), respectively. Therefore, it could be possible to say that these sediments are mostly polluted via the discharge from river.

At the spot No. 1, total nitrogen contents are higher than two other spots by three times. Organometallic nickel is no parallel to nitrogen contents.

Ni/N indices are feasible to conclude relatively to be close to that of oil.

TABLE 4

Determinatiion of Total Organic Nitrogen and Organometallic Nickel in the Hexane Extracts of Marine Products after Saponification and Ni/N Indices

Samples	Source	ppm(whole base) Total Organic Nitrogen	ppm(whole base) Organometallic Nickel	Ni/N Indices*1
Clam	Ehime	3.05	0.010	3.2
(*Meretrix*)	Ehime	2.26	0.005	2.2
	(Kyusyu)	3.93	0.003	0.7
	(Korea)	3.28	0.001	0.3
Short-necked	Mie	12.1	0.004	0.3
clam(*Tapes*)	Shizuoka	5.28	0.004	0.7
Corbicula	Mie	6.64	0.003	0.5
(*Corbicula*)	Shimane	2.99	ND	---
Turban shell	Ishikawa	3.75	0.017	4.5
(*Turbo*)	(shellfish)			
	Ishikawa (intestine)	7.27	0.063	8.6
	Yamaguchi	3.88	0.017	4.3
Scallop	Aomori	4.78	0.008	1.6
(*Pecten*)	Aomori	4.96	0.004	0.8
Ear shell	Tokushima	4.89	0.014	2.8
(*Haliotis*)				
Ark shell	Mie	5.98	0.019	3.1
(*Arca*)				
Oyster	Hiroshima	6.95	0.003	0.4
(*Crassostrea*)	Hiroshima	2.16	0.027	12.5
	Hiroshima	2.62	0.005	1.9
	Hiroshima	2.34	0.016	6.8
*Cella stearnsii**2	Osaka	9.55	0.013	1.3

ND < 0.001 ppm,

*1; Organometallic Nickel/ Organic Nitrogen X 10^3

*2; collected directly in the estuary of Osaka Bay, 1977.

Table 4 shows the total organic nitrogen and organometallic nickel after saponification in marine samples, mainly shellfishies.

From the data by IKEBE and TANAKA (1979), total contents of nickel including inorganic and organic nickel are 10-1000 times as much as organometallic nickel in these marine samples.

Average contents of nickel in the shellfish of turban shell(*Turbo*), for instance, are 0.183 ppm(range;0.304-0.520), organometallic nickel analysed is 0.017 ppm, while nickel content in the intestine is 0.980 ppm(range;0.738-1.53), organometallic one is 0.063 ppm.

As for clam(*Meretrix*), average contents of nickel are 0.868 ppm(range;0.536-1.11), while organometallic one is 0.022 ppm(range; 0.001-0.010).

Ni/N indices of marine samples are much lower comparing with that of heavy oils and sediments, excepting turban shell(intestine); 8.7, and one oyster sample;12.5.

Consequently, it could be possible to conclude that higher contaminated samples such as sediments and/or marine samples polluted just after oil spillage would identified by these indices.

These indices, therefore, could clarify some fingerprints of oil contamination with the combination of other components such as organic sulfur containing oil compounds in marine products.

Since the profiles of other organometallic compounds in petroporphirins such as vanadium are less reported, chemo-toxicological implications of these compounds are being studied.

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