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Determination of Vanadium in a Marine Mollusc Using a Chelating Ion Exchange Resin and Neutron Activation*

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Studies designed to measure contaminants in the marine and estuarine environment have generally neglected vanadium. Environmental vanadium has been considered as a trace constituent of petroleum which has levels ranging, for example, from 0.6 to 1400 ppm in different Venezuelan crude oils (NAS 1974). Variable vanadium concentrations characterize different petroleums; such "fingerprints" in oil spill samples have been useful in establishing responsibility for pollution incidents (GUINN et al.1971).

While vanadium is an essential element for man (HOPKINS and MOHR 1974), it is toxic in excessive amounts, as it interferes with various enzyme systems (NAS 1974).

Due to its generally low concentration in marine molluscs (< 1µg/g dry wt.) and the current widespread use of bay mussels, *Mytilus edulis*, as environmental monitors, it is necessary to utilize a sensitive analytical method for its determination. Flameless AA has been commonly employed (IKEBE and TANAKA 1979) and has the advantage of being widely available. Neutron activation analysis (NAA) is more sensitive when a source of thermal neutrons is available. A primary problem with utilizing NAA for vanadium determinations is the necessity of separating sodium from biological matrices because of high Compton contribution from ^{24}Na when purely instrumental procedures are employed (BLOTCKY et al. 1979). GUINN et al. (1977) removed sodium from a biological matrix by using a column containing hydrated antimony pentoxide; unfortunately, antimony then became a contaminant which provided its own Compton contribution. Nevertheless, they demonstrated that much greater sensitivity could be attained with their procedure. RILEY and TAYLOR (1968) used a chelating resin for separating vanadium from seawater and KINGSTON et al. (1978) used the same resin to separate eight other transition elements from seawater.

The purpose of the present study was to develop a precise

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method for measuring vanadium in the soft tissue of marine molluscs. We employed a chelating resin to retain vanadium and eliminate sodium from a digest of the soft tissues of *M. edulis*. Vanadium concentrations were then obtained via neutron activation analysis of the resin which retained the vanadium.

MATERIALS AND METHODS

Sample Preparation. Samples of *M. edulis* were collected from a site on Yaquina Bay (Newport, OR) and transferred to our laboratory at O.S.U. Preparation consisted of shucking (removal of the animal from the shell), homogenizing, and either wet digestion or freeze-drying.

Digestion. Approximately 3 g (wet wt.) of homogenized tissue were placed into a screw-top culture tube (150 x 25 mm) and 4 mL conc HNO_3 (reagent grade) was then added. The tube was tightly capped and placed in a heat block at 90°C for approximately 1 h. After completion of digestion, the digest was filtered through glass wool and made up to a volume of 10 mL with 18 MΩ cm distilled water.

Freeze-drying. Homogenized tissue was freeze-dried for 48 h at a pressure of 90 mtorr. Residual moisture was determined by drying to constant weight at 100°C. Freeze-drying permitted the use of a larger sample size for instrumental neutron activation analysis (INAA). Approximately 0.5 g of dried tissue was heat-sealed in a 2/5 dram polyvial which was in turn heat-sealed in a 2 dram polyvial, providing double containment to reduce the likelihood of contamination.

Column Separation. Polypropylene columns (60 x 8 mm I.D.) were acid-washed and filled with a slurry of Chelex 100 resin (Bio-Rad, analytical grade, sodium form), 200-400 mesh. The columns were then rinsed with 2 x 5 mL volumes of 2.5 M HNO_3 followed by 2 x 5 mL volumes of 2.0 M NH_4OH, and 2 x 5 mL volumes of distilled water, pH 5.1. This procedure removed any metal contaminants.

A 1 mL aliquot of the digest solution (above) was further diluted with 20 mL of distilled water, pH 5.1, and its pH adjusted to pH 5.1 with conc. NH_4OH. The digest solution was then added to the column reservoir and alkali metals were eluted off the resin with 4 x 5 mL volumes of 1.0 M ammonium acetate. The resin from each column was then double contained as above.

Activation and Sample Counting. The neutron source was the 1 MW TRIGA research reactor at the O.S.U. Radiation Center. A pneumatic tube sample placement system (rabbit) was employed which located the sample at a point where the neutron flux at full power (1 MW) was 9.0×10^{12}n $cm^{-2}s^{-1}$. Sample counting equipment con-

sisted of a 2048 channel analyzer (Nuclear Data Corp. ND-600) interfaced with a 15% Ge(Li) detector. Two different procedures were used: (1) INAA samples were irradiated for 30 s at 200 KW and counted for 60 s after a delay time of 3 min. (2) Resin samples were irradiated for 60 s at 1 MW and counted for 5 min after a delay of 4 min.

RESULTS & DISCUSSION

Counting reagent blanks has shown that vanadium is not a constituent of the background contaminants at our facilities, nor was it detected in the reagents or polyvials used. While columns and glassware are customarily washed in 50: 50 HNO_3 (~24 h) this does not appear to be essential.

Transfer of polyvials after activation minimizes the contribution of ^{41}Ar and ^{28}Al to the background. The former is of atmospheric origin and the latter is a contaminant of the polyethylene vials used.

TABLE I compares vanadium levels determined by the two methods in 5 different tissue samples of *M. edulis*. Samples SA-1, -4, -7 and -10 each consisted of the pooled soft parts of 20 animals from which the gonads had been removed. Sample GA-7 was the pooled gonads of 20 animals obtained in preparation of sample SA-7. No other sample of gonadal material contained a detectable level of vanadium.

TABLE I. Vanadium levels in five samples of soft tissue of *Mytilus edulis* and two NBS standards. The vanadium concentrations obtained with an INAA procedure are compared with concentrations determined after eliminating sodium from the matrix. Vanadium was retained on Chelex 100 and sodium eluted off the resin. Concentrations and standard deviations are in µg/g.

Sample	INAA	CHELEX 100 & NAA
SA-1	1.66 ± 0.47 (28.3%)	0.84 ± 0.07 (8.3%)
SA-4	0.67 ± 0.26 (38.8%)	1.06 ± 0.09 (8.5%)
SA-7	2.75 ± 0.69 (25.1%)	0.82 ± 0.05 (6.1%)
SA-10	2.21 ± 0.51 (23.1%)	1.03 ± 0.08 (7.8%)
GA-7	0.49 ± 0.23 (46.9%)	0.30 ± 0.04 (13.3%)
NBS Orchard Leaves	1.13 ± 0.28 (24.8%)	--
NBS Oyster Tissue	--	2.24 ± 0.08 (4.0%)

Vanadium recovery for digestion followed by column separation was determined from two tissue samples fortified with 1.0 µg of vanadium and was found to be 89 ± 12%. The uncertified value for NBS Oyster Tissue is given (NBS Standard Reference Material 1566)

as 2.8 µg/g, and the value of 2.24 µg/g in TABLE I represents a recovery of 80%.

The use of NBS Orchard Leaves (NBS Standard Reference Material 1571) verified that the INAA method standard deviations are also much larger than those obtained after separation of vanadium with Chelex-100. BLOTCKY et al. (1979) found the vanadium content of NBS Orchard Leaves to be 0.60 ± 0.02 µg/g. NBS does not certify a value for this reference material.

In attempting to employ a strictly instrumental procedure (INAA) with biological material, the high background caused by ^{24}Na dictates the use of low reactor power levels, which are difficult to maintain without variation in neutron flux. Irradiation times must be short for the same reason. Thus, the measurement of small quantities of vanadium (< 2 ppm) in biological material without chemical separation becomes difficult or impossible. The preirradiation elimination of sodium and retention of vanadium in a resin matrix, as we have described, permits activation at full reactor power. Further, irradiation time is not critical and may be as long as is convenient, with an accompanying reduction of timing errors. The use of full reactor power can represent an economic advantage, as expensive facilities need not be allocated to strictly low-power operations. Long activations which customarily require full power operation can be run concurrently with the regime we have suggested. An additional background problem arises when samples are counted. A large background contribution necessitates short counting times. If long counting times are attempted, peaks of interest may become overshadowed. This tendency was noted when an attempt was made to count INAA samples for longer than 60 s.

REFERENCES

BLOTCKY, A.J., C. FALCONE, V.A. MEDINA, E.P. RACK and D.W. HOBSON: Anal. Chem. *51*, 178 (1979).

GUINN, V.P., D.E. BRYAN and H.R. LUKENS: *Nuclear Techniques in Environmental Pollution.* International Atomic Energy Agency, Vienna. pp. 347-359 (1971).

GUINN, V.P., E.R. CHRISTENSEN, K. DE LANCEY, W.W. WADMAN III, J.H. REED, N. HANSEN, A. ABU SAMRA and V.J. ORPHAN: *Nuclear Methods in Environmental Research.* CONF-771072-. pp. 303-311 (1977).

HOPKINS, L.L. and H.E. MOHR: Fed. Proc. *33*, 1773 (1974).

IKEBE, K. and R. TANAKA: Bull. Environ. Contam. Toxicol. *21*, 526 (1979).

KINGSTON, H.M., I.L. BARNES, T.J. BRADY and T.C. RAINS: Anal. Chem. *50*, 2064 (1978).

NAS: *Medical and Biologic Effects of Environmental Pollutants: Vanadium.* National Academy of Sciences, Washington, D.C. 117 pp. (1974).

RILEY, J.P. and D. TAYLOR: Anal. Chim. Acta *41*, 175 (1968).