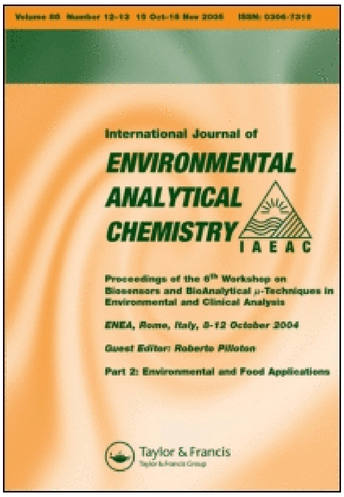

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Suzuki, Nobuo , Iwata, Yoshihiro and Imura, Hisanori(1987) 'Determination of Several Trace Metals in Seaweed by Neutron Activation Analysis after Diethyldithiocarbamate Extraction and Polystyrene-foam Collection', International Journal of Environmental Analytical Chemistry, 30: 4, 289 — 297

To link to this Article: DOI: 10.1080/03067318708075477

URL: http://dx.doi.org/10.1080/03067318708075477

Intern. J. Environ. Anal. Chem., 1987, Vol. 30, pp. 289–297
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Printed in Great Britain

Determination of Several Trace Metals in Seaweed by Neutron Activation Analysis after Diethyldithiocarbamate Extraction and Polystyrene-foam Collection

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(*Received December 15, 1986; in final form March 3, 1987*)

Traces of vanadium, iron, cobalt, nickel, copper, and zinc were quantitatively extracted with diethyldithiocarbamate (DDTC) in benzene from a wet-ashed solution of a seaweed at pH 3.2–5.5 and manganese was completely extracted at pH 4.5–7.7. The metal–DDTC complexes extracted were quantitatively collected with a polystyrene foam produced by lyophilization of the benzene extract after an addition of polystyrene. The foam was pelletized and subjected to neutron activation analysis. This method was applied to seaweed samples and six trace metals were simultaneously and accurately determined.

KEY WORDS: First transition metals, neutron activation analysis, solvent extraction, polystyrene foam, preconcentration, biological material.

INTRODUCTION

It is well known that most of the first transition metals are essential elements for almost all organisms and are involved in organisms in trace level as often sub-ppm level. Although the neutron activation analysis (NAA) has excellent sensitivity for the determination of those elements, a nondestructive γ-ray spectrometry cannot be very often performed especially in the case of biological samples because of the production of interfering radionuclides, e.g., γ-ray measurement of ^{64}Cu (half life, 12.7 h; γ-peak, 1346 keV) cannot be done in the presence of high activity of ^{24}Na (half life, 15.0 h; γ-peak, 1369 keV), and also the measurement of other nuclides of trace elements is remarkably interfered by very high back-ground activity of ^{24}Na, ^{38}Cl, ^{80}Br, and ^{82}Br, which are induced from large amounts of alkali and halogen elements. Such interferences inherent in NAA for biological materials have been pointed out in a recent review,[1] that is, the high γ-activities due to the major elements limit the sensitivity of the method of many trace elements with comparable or shorter lived radioisotopes. Actually in a literature dealing with the nondestructive NAA for several marine organisms,[2] no data have been given for vanadium, manganese, and copper. In addition, only an upper limit has been given for zinc in algae and angiospermae probably due to low sensitivity of this element in NAA. These are also serious problems in the radioactivation analysis of our seaweed samples, that is, Laminaria religiosa and Sargassum horneri contain 2–5% sodium, 8–19% chlorine, 0.04–0.08% bromine, and 0.05–0.3% iodine.[3] Hence chemical separation methods for trace metals are inevitable to obtain reliable results. Furthermore, for the determination of very trace level of metals, an appropriate preconcentration procedure must be introduced. Several preconcentration methods using solid adsorbents such as chelating polymers,[4,5] ion exchanger,[6] and coprecipitator[7] have been utilized. The solvent extraction is a simple and powerful separation method and many research works on the solvent extraction of various metals with different chelating agents have been made, but very few research work of the solvent extraction combined with the radioactivation analysis of trace metals has been appeared,[8] and this is mainly due to a susceptible extractability of trace metals from a crude matrix solution of bio- and geological samples, and due to a difficulty to prepare a limited volume of the target for neutron irradiation from a large volume of the organic extract resulted from the solvent extraction separation.

In the present investigation, we develope a preseparation–preconcentration method for NAA of seven first transition metals, vanadium, manganese, iron, cobalt, nickel, copper, and zinc. This method involves the selective and quantitative extraction of these metals with diethyldithiocarbamate (DDTC), and followed by the concentration and collection of these extracted metal complexes using polystyrene foam produced by lyophilization. The present preseparation–preconcentration method combined with NAA is applied to seaweed samples.

EXPERIMENTAL

Reagents

Radioisotopes, ^{48}V, ^{54}Mn, ^{59}Fe, ^{57}Co, ^{57}Ni, ^{67}Cu, and ^{65}Zn, were used; ^{48}V was produced by the $^{48}Ti(p,n)^{48}V$ reaction with 18 MeV protons from a cyclotron of Tohoku University and isolated from the target with DDTC extraction;[9] ^{59}Fe was produced by the neutron irradiation of iron(III) oxide for 12 d with JRR-2 in Japan Atomic Research Institute and dissolved in hydrochloric acid; ^{57}Ni and ^{67}Cu were produced by $^{58}Ni(\gamma,n)^{57}Ni$ and $^{68}Zn(\gamma,p)^{67}Cu$ respectively with 50 MeV bremsstrahlung from an electron linear accelerator of Tohoku University. The nickel oxide target was dissolved in hydrochloric acid and ^{67}Cu was isolated from the zinc target with DDTC extraction;[10] carrier-free ^{54}Mn, ^{57}Co, and ^{65}Zn were obtained from the New England Nucl. Co.

Sodium diethyldithiocarbamate was of a guaranteed reagent grade, dissolved in redistilled water to be 0.2 M solution and purified by washing with carbon tetrachloride at pH 9 to remove extractable metal impurities just before use. The 0.1 M DDTC solution in 0.1 M sodium hydroxide was prepared. The 5% polystyrene-benzene solution was prepared using polystyrene of polymerization degree 1600–1800 and purified by successively washing with 6 M hydrochloric acid, 0.1 M ethylenediaminetetraacetic acid (pH 8–10), and redistilled water. The 0.5 M tartaric acid solution was purified by adding appropriate amount of the 0.2 M DDTC solution and washing with carbon tetrachloride. Benzene and carbon tetrachloride were purified by the ordinary methods. Sodium hydroxide and sodium acetate were super high purity reagents (Merk, Suprapur) and acids used also super high purity reagents (Wako Pure Chem.). Unless otherwise stated, the reagents were of analytical reagent grade.

Preparation of seaweed samples

Seaweed samples, Laminaria religiosa Miyabe, were obtained from Onagawa bay, Miyagi prefecture Japan, in November 1982. The samples were kept at below −20°C immediately after collecting and washing with filtered sea water. Then they were subjected to the lyophilization for 48 h and powdered using an agate mortar. The analytical sample was dried for 2 h at 85°C before use.

Recommended procedure for determination of trace metals

One gram of a seaweed sample was placed in a decomposition vessel (UNISEAL, 70 ml) and 10 ml of concentrated nitric acid was added. The vessel was heated for 3–4 h at 150°C. After cooling, the contents were evaporated to dryness and dissolved in 9 ml of 0.04 M acetate buffer (pH 4–5) containing 0.02 M tartrate. Then the aqueous solution was put into a 50-ml extraction tube with a ground glass stopper containing 10 ml of benzene. Immediately after addition of 1 ml of the 0.1 M DDTC solution, the contents were vigorously shaken for 10 min and centrifuged. The organic extract was taken out. After adjusting the pH value of the remaining aqueous phase to 5–7.5, another 1-ml portion of 0.1 M DDTC was added and shaken again with 10 ml of benzene. In the first extraction, vanadium, iron, cobalt, nickel, copper, and zinc are extracted, and in the second extraction, manganese being extracted. To the total extract obtained by the duplicate extraction was added 2 ml of the 5% polystyrene solution in benzene. Then the benzene solution was frozen using liquid nitrogen and subjected to the lyophilization to remove benzene. The resulting polystyrene foam (0.1 g) including the metal-DDTC complexes was pelletized into discs with a 10-mm diameter. As a comparative standard for NAA, a synthetic multielement reference material with polyacrylamide gel matrix containing known quantities of metal ions of interest (vanadium, 10.6 μg; manganese, 0.763 μg; iron, 85.1 μg; cobalt, 0.680 μg; nickel, 40.9 μg; copper, 43.1 μg; zinc, 36.1 μg) was prepared[11,12] and pelletized into discs of the same geometry with the polystyrene form disc from the sample. The sample and the comparative standard discs were separately sealed in small polyethylene bags, put into a polyethylene capsule and irradiated for 10 min with thermal neutron (flux, $5.4 \times 10^{13}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) in JRR-2 of Japan Atomic Research Institute. Gamma-ray spectra were measured with a Ge(Li) or Ge semiconductor detector connected with 4096 channel pulse height analyzer at various intervals over periods from 15 min to 2 weeks after irradiation. Each element was determined by the photo-peak area of γ-ray of the corresponding nuclide, i.e., ^{52}V(1434 keV), ^{56}Mn(847 keV), ^{59}Fe(1099 keV), ^{60}Co(1173 keV), ^{65}Ni(1482 keV), ^{64}Cu(1346 keV), and ^{65}Zn(1116 keV).

RESULTS AND DISCUSSION

Extraction of trace metals with diethyldithiocarbamate

The DDTC extraction of a series of first transition metals such as vanadium, manganese, iron, cobalt, nickel, copper, and zinc from a digested seaweed solution containing large amounts of alkali, alkaline earth, and halogen elements was investigated. An aliquot of each radioactive tracer was spiked to the digested solution obtained by the wet-ashing of seaweed with concentrated nitric acid, and the extraction with 0.01 M DDTC into benzene was carried out at various pH of the digested solution. The γ-activity of the organic phase was measured and the extraction percent was calculated. Figure 1 shows the extraction curves of the metal ions from the digested solution after an addition of 0.02 M tartrate to prevent hydrolysis of these metals. Vanadium, iron, cobalt, nickel, copper, and zinc are quantitatively extracted at pH 3.2–5.5 and manganese at pH 4.5–7.7. This pH range for quantitative extraction is not so different from that of an ordinary DDTC extraction of these metals from simple aqueous solution not containing diverse ions.[13,14] When tartrate was absent, the extraction of manganese and iron was remarkably lowered at above pH 4 due probably to hydroxide formation. All of these metal ions of interest can be simultaneously extracted at pH 4.5–5.5, but, instead of the careful adjustment of pH of the acid digested sample solution to this narrow pH range, it is practical to apply the duplicate extractions at pH 3.5–5.0 and pH 5.0–7.5.

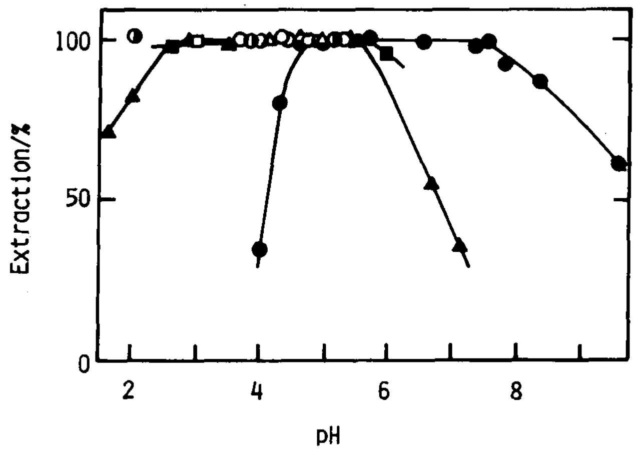

Figure 1 Extraction of trace metals with 0.01 M diethyldithiocarbamate into benzene from wet digested solution of seaweed sample. Radioisotopes, ^{48}V, ^{54}Mn, ^{59}Fe, ^{57}Co, ^{57}Ni, ^{67}Cu, and ^{65}Zn were spiked. Tartrate, 0.02 M; shaking time, 10 min. ▲, V; ●, Mn; ■, Fe; □, Co; ◑, Ni; ○, Cu; △, Zn.

Collection of the extracted metals with polystyrene foam

Solvent extraction is very good method to separate metal ions of interest with a high efficiency, but a quite large volume of the organic extract thus obtained is troublesome to be applied to NAA. Here the collection with polystyrene foam was investigated. A benzene solution of the radioactive metal-DDTC complexes was prepared by extracting corresponding radioactive tracer with DDTC. To 3 ml of this solution was added a 0.3 ml portion of 5% polystyrene in benzene and lyophilized to remove benzene solvent. The γ-activity of the residue (polystyrene foam) was measured after pelletizing into discs with the same dimension. As is summarized in Table I the recovery of all metals is better than 99%. The metal-DDTC complexes are quantitatively retained in the polystyrene foam during the lyophilization without any loss due to volatilization and/or adsorption of the complexes on the wall of glass vessel. According to the recommended procedure, the DDTC complexes extracted into 20 ml benzene can be readily concentrated into 0.1 g of the polystyrene foam, and this means that nearly 200 times of enrichment of trace metals is achieved at this collection. The

Table I Collection of metal-DDTC complexes with polystyrene foam

Element[a]	Recovery/%	(n)
V	100.0 ± 0.8	(3)
Mn	100.1 ± 0.5	(3)
Fe	99.7 ± 3.0	(3)
Co	100.6 ± 0.5	(3)
Cu	99.6 ± 0.4	(3)
Zn	100.1 ± 1.1	(3)

[a] 0.3 μg of element.

form can be readily pelletized by hand pressure, and the polystyrene foam with the same geometric shapes are obtained from the analytical sample and the comparative standard, and this may minimize an error in the radioactivity measurement.

Application to seaweed sample

To examine the reliability of the present idea, the present method was applied to a synthetic reference material having a similar matrix and elemental composition with a seaweed as shown in Table II.[3,11,12] Analytical results for a series of first transition metals in this synthetic reference material are summerized in Table III. By comparing the analytical results in Table III with the corresponding original content in the synthetic reference material in Table II, it is clearly seen that these trace metals of interest are accurately and precisely determined under 8% of the relative error observed for iron and also 8% of the relative standard deviation for cobalt. Here the relative error expressed in percentage is defined as the ratio of the difference between the known content of an element (Table II) and the determined value (Table III) against its known content. The trace amount of nickel as 1 μg/g could not be detected due to its low sensitivity in NAA even after enrichment from 1 g of the synthetic reference material. The blank experiment was performed by the same procedure, and mere trace amount of manganese, 0.036 μg, was determined as a blank value, but other metals were not at all. Thus the blank values were to be negligible.

Table IV shows the determined values of six trace metals in a

Table II Elemental composition of a synthetic reference material[a]

Element	Content/%	Element	Content/$\mu g \cdot g^{-1}$
C	39.9	Al	158
H	6.7	V	2.72
N	3.4	Cr	0.673
O	34.7	Mn	3.13
		Fe	38.9
Na	3.26	Co	0.238
Mg	1.05	Ni	1.04
P	0.131	Cu	1.27
S	0.13	Zn	24.8
Cl	5.83	As	125
K	6.44	Br	858
Ca	1.09	Rb	11.7
I	0.224	Sr	510

[a] Elemental composition is adjusted to be similar to that of a seaweed.[3,11,12]

Table III Determination of trace metals in a synthetic reference material

Element	Found/$\mu g \cdot g^{-1}$	(n)
V	2.76±0.13	(3)
Mn	3.28±0.20	(3)
Fe	35.6±1.5	(3)
Co	0.253±0.017	(3)
Ni	Not detected	
Cu	1.3±0.1	(3)
Zn	25.6±1.7	(3)

Table IV Multielement analysis of a seaweed, Laminaria religiosa Miyabe, by the preseparation-neutron activation analysis

Element	This work[a]	(n)
V	2.60±0.14 (2.49±0.23)[b]	(3)
Mn	3.20±0.19	(3)
Fe	36.4±2.6	(3)
Co	0.196±0.011	(3)
Cu	0.64±0.02 (0.69±0.05)	(3)
Zn	25.1±1.4 (24.4±0.4)	(3)

[a] μg/g, dry weight.

[b] Zeeman atomic absorption spectrometry,[15] μg/g.

seaweed, Laminaria religiosa Miyabe. Comparative data for these elements in the present seaweed have not been reported yet, only a few data for vanadium, copper, and zinc determined by an atomic absorption spectrometry are also shown in this table.[15] A good agreement among these data is clearly observed. It is difficult to show the detection limits uniquely, since they strongly depend on the experimental conditions and the matrix nature. In this work, the practical detection limits were estimated based on the γ-ray spectral data of the irradiated synthetic reference material with pseudo-biological matrix composition shown in Table II as an example. The detection limit is defined as 3σ (standard deviation) of the γ-ray counts of base line at a photo peak used for the determination of each metal; these are 9.8 ng for vanadium, 5.8 ng for manganese, 1.0 μg for iron, 2.4 ng for cobalt, 46 ng for copper, and 170 ng for zinc at the present experimental condition. The present method using a preseparation–preconcentration method combined with NAA can be applied to the simultaneous determination of trace amounts of first transition metals in other biological materials.

References

1. R. Cornelius, J. Hoste and J. Versieck, *Talanta* **29,** 1029 (1982).
2. M. Martić, N. Ajdačić, J. Stjepčević and M. J. Gašić, *J. Radioanal. Chem.* **59,** 445 (1980).
3. N. Suzuki, Y. Iwata, H. Imura and K. Masumoto, *Res. Rept. Nucl. Sci. Tohoku Univ.* **16,** 126 (1983).
4. A. Hirose, K. Kobori and D. Ishii, *Anal. Chim. Acta* **97,** 303 (1978).
5. S. Imai, M. Muroi, A. Hamaguchi and M. Koyama, *Anal. Chem.* **55,** 1215 (1983).
6. A. Hirose and D. Ishii, *J. Radioanal. Chem.* **45,** 305 (1978).
7. J. Holzbecher and D. E. Ryan, *J. Radioanal. Chem.* **74,** 25 (1982).
8. J. M. Lo, J. C. Wei and S. J. Yeh, *Anal. Chim. Acta* **97,** 311 (1978).
9. N. Suzuki, M. Takahashi and H. Imura, *Anal. Chim. Acta* **160,** 79 (1984).
10. H. Imura and N. Suzuki, *J. Radioanal. Nucl. Chem.* **88,** 63 (1985).
11. K. Masumoto and N. Suzuki, *Radiochem. Radioanal. Lett.* **42,** 99 (1980).
12. N. Suzuki, Y. Iwata and H. Imura, *Anal. Sci.* **2,** 335 (1986).
13. H. Bode and F. Neumann, *Z. Anal. Chem.* **172,** 1 (1960).
14. T. Honjo and H. Imura, *Bull. Chem. Soc. Jpn.* **53,** 1753 (1980).
15. M. Kikuchi, H. Imura and N. Suzuki, The 46th Symposium on Analytical Chemistry (The Japan Society for Analytical Chemistry), Koriyama, 1985.