ACTIVATION ANALYSES OF VANADIUM, ARSENIC, MOLYBDENUM, TUNGSTEN, RHENIUM, AND GOLD IN MARINE ORGANISMS[1]

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ABSTRACT

Activation analyses have been carried out for 6 trace elements—vanadium, arsenic, molybdenum, tungsten, rhenium, and gold—in the ashes of several different types of marine organisms. Radiochemical procedures coupled with gamma-ray measurement permitted unambiguous determination of submicrogram amounts of these elements. No reagent blank corrections were needed. Experimental sensitivities for each element are given.

INTRODUCTION

Many studies have been made on the abundance of trace elements in marine organisms. Early data have been summarized in Vinogradov's (1953) comprehensive compilation and current periodicals continually supplement this information. Nevertheless, systematic studies of trace element abundance are far from complete because of the inherent difficulties in the analytical methods and because of the many varieties included in the category of marine organisms. The importance of these studies has been emphasized in the last decade in connection with the radioactive contamination caused around the Equatorial Pacific by atomic explosions. The cycle of trace elements in marine organisms has become an important basic problem to be solved early in the atomic age because of questions arising from the disposal and dispersal of radioactive wastes in the sea.

In the past spectrographic and spectrophotometric methods have been widely applied to these trace element studies. These methods are, however, restricted for some elements in this type of sample because of insufficient sensitivity and large reagent blanks. Activation analysis can overcome these disadvantages in many cases since it has excellent sensitivity for many elements for which the conventional methods present difficulties. In addition, problems of reagent blanks are eliminated. Therefore, activation analysis should play an important role in supplying complementary or unknown information on trace elements in marine organisms (Fukai and Meinke 1959a).

Bowen (1956) has applied activation analysis to various types of marine samples and sea water to determine strontium and barium. Rubidium and cesium in sea water and seaweeds were analyzed by Smales and Salmon (1955) using this method. Among these elements, the newly obtained abundance of barium and cesium was less by a factor of 10 than the previously accepted value. Activation analysis has also been applied to the estimation of arsenic (Smales and Pate 1952), gold (Hummel 1957), and uranium (Stewart and Bentley 1954) in sea water, although these measurements were not extended to biological materials.

In order to re-examine existing data and to obtain new information, ashes of 6 different marine samples have been analyzed for vanadium, arsenic, molybdenum, tungsten, rhenium, and gold by activation analysis (Fukai and Meinke 1959b).

Recently the authors (1959a) compiled from existing data a generalized table for the average abundance of trace elements in marine organisms and in sea water. In this table the four groups, seaweeds, mollusks, crustaceans, and fishes, were chosen as representative while sea water was added as the source of the trace elements contained in these organisms. It is difficult to

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TABLE 1. *Average abundance of the 6 trace elements in marine organisms and sea water on the basis of existing data (Fukai and Meinke 1959a)*

Atomic No.	Element	Seaweeds g/g dried matter	Mollusks (without shell) g/g dried matter	Crustaceans (without carapace) g/g dried matter	Fishes (soft parts) g/g dried matter	Sea water g/g water
23	Vanadium	2×10^{-6}	1×10^{-6}	5×10^{-7}	2×10^{-7}	3×10^{-10}
33	Arsenic	3×10^{-5}	4×10^{-6}	5×10^{-6}	7×10^{-6}	3×10^{-9}
42	Molybdenum	5×10^{-7}	2×10^{-6}	5×10^{-7}	5×10^{-7}	(5×10^{-10})
74	Tungsten	+	—	—	—	1×10^{-10}
75	Rhenium	±	—	—	—	—
79	Gold	(1×10^{-6})	—	—	1×10^{-8}	3×10^{-11}

+ = element has only been detected; ± = detection uncertain; — = element has not been detected or reported; ( ) = less reliable values; figures underlined are those obtained by activation analysis.

obtain an average abundance of an element for a classification of this kind, since each group includes a number of species and since the abundance of some elements varies widely among species. Nevertheless, it is possible from this compilation to get a general idea of the abundance in a particular group which can be used as a starting point for further detailed studies.

In Table 1 the average abundances are given from this compilation (Fukai and Meinke 1959a) for the 6 elements dealt with in the present paper. It can be seen that considerable information is available for vanadium, arsenic, and molybdenum, while only a few values have been reported for tungsten, rhenium, and gold.

Table 2 summarizes the nuclear characteristics of the radioisotopes of the 6 elements

used in the neutron-activation analysis. Two elements, vanadium and technetium, required work with rather short half-lived radioisotopes while the other four allowed more time for the analyses.

METHODS

Collection and preparation of the samples

The samples analyzed were collected around the coast or in the vicinity of the main island of Japan from 1956 to 1958. The ash samples were prepared by igniting dried marine organisms in a quartz crucible at a temperature below 550°C. Consequently, there may be a possibility of losing some part of the desired elements in this step. However, from checks made by using radioisotopes, it may be concluded that the loss of the desired elements rarely exceeds

TABLE 2. *Nuclear properties[1] of the radioisotopes measured and conditions of the irradiations*

Element	Vanadium	Arsenic	Molybdenum	Tungsten	Rhenium	Gold
Atomic No.	23	33	42	74	75	79
Isotope (parent)	V^{51}	As^{75}	Mo^{100}	W^{186}	Re^{185}	Au^{197}
Abundance (%)	99.75	100	9.62	28.4	37.07	100
Thermal neutron cross section (barns)	4.5	4.2	0.2	34	100	96
Daughter product	V^{52}	As^{76}	$*Tc^{101}$	W^{187}	Re^{186}	Au^{198}
Half-life of daughter	3.8 min	26.5 hr	14.0 min	24.0 hr	3.7 day	2.7 day
Gamma-energy for gamma-spectroscopy (Mev)	1.44	0.56	0.307	0.072	0.137	0.412
Type of irradiation	Pneumatic tube	Pool	Pneumatic tube	Pool	Pool	Pool
Reactor power level (kw)	100	100	1000	1000	1000	1000
Irradiation period	10 min	5–9 hr	15 min	6.3 hr	11.5 hr	14.1 hr
Average neutron flux (n cm^{-2} sec^{-1})	9×10^{10}	7×10^{11}	9.4×10^{11}	1.5×10^{12}	3.5×10^{12}	2.5×10^{12}

[1] Strominger, Hollander, and Seaborg 1958; Hughes and Harvey 1955.

* This isotope is the daughter of Mo^{101}.

10%, although the degree of the loss varies depending on the chemical property and state of the elements. On the other hand, contamination of the samples from the surroundings was carefully avoided. In the case of mollusks there may be a possibility of contamination, since it was difficult to remove all of the microscopic grains of mud or sand from the digestive tracts. In the other cases, however, the degree of contamination should be insignificant.

Apparatus

All neutron irradiations were carried out with the Ford Nuclear Reactor of the University of Michigan and the associated facilities of the Michigan Memorial Phoenix Project (Meinke 1959). Short irradiations were made at the side of the reactor core by means of a pneumatic tube system. Samples were contained in a quick-opening plastic "rabbit" which was irradiated in this system at thermal neutron fluxes of about 10^{12} neutrons cm^{-2} sec^{-1} and delivered to a hood for chemical processing within 3 sec after irradiation. The radiochemical separations were then performed immediately.

When relatively long-lived isotopes were to be measured, in-pool irradiations were made by using polyethylene containers or aluminum cans plus a suitable weight suspended by aluminum wires. After these pool irradiations, the samples were set aside for a while to "cool" to reduce the radiation hazard encountered in the processing.

After separation, samples were measured by a 3 × 3-in. NaI (Tl) scintillation crystal coupled with a 100-channel pulse-height analyzer with duplicate memories or followed for decay with a scintillation well counter (1 × 1½-in. NaI (Tl) crystal). This equipment has been described in detail elsewhere (Meinke 1957, 1958, 1959).

Irradiation procedures

About 500 mg of the ash samples were taken for each analysis except for vanadium and molybdenum, where 50–100 mg and 200–250 mg, respectively of the ash were used. The ashes taken were sealed in clean polyethylene or aluminum envelopes; suit-able foils for monitoring the neutron flux were attached to both sides of each envelope. Aluminum envelopes (made from 5-mil. aluminum foil) were used only for the pool irradiations. Usually about 1 mg of 1-mil. gold foil was used as the flux monitor in the short irradiations for vanadium and molybdenum, while 5–10 mg of 2-mil. aluminum-cobalt foil were employed for the longer irradiations for the other elements. The cobalt content of the aluminum-cobalt foil had previously been determined by activation analysis based on Co^{60m} activity and gamma-ray spectroscopy.

General analytical steps

After irradiation of the sample and any required "cooling," the irradiated ashes were dissolved in hot acidic or basic solution and radiochemical separations performed to purify the isotope desired. Solvent extraction was preferred for this separation, since in many cases it accomplishes clean separations within a relatively short period of time. Since the main purpose of the separation was to reduce the activity from contaminating radioisotopes so as to make gamma-ray spectroscopy possible, the separation of the radioisotope did not have to be quantitative. In biological ash samples the contaminating activity consists mainly of Na^{24} and P^{32} and it was not difficult to reduce this activity by simple solvent extraction.

The purified samples were then usually measured by the scintillation detector to determine the amount of characteristic gamma-rays present from the radioisotope in question. For short-lived isotopes the changes in the gamma-spectrum were followed continuously by using the dual memories of the pulse-height analyzer and recycling the counting period to observe the characteristic half-life of the gamma-ray peak. Verification of the desired radioisotope was based on both the gamma-ray energy and the half-life measurements. Amounts of the desired radioisotope present were determined by the area under the photopeak of the gamma-ray spectrum. Analysis of the spectra obtained for the

longer-lived isotopes was essentially the same, although the decay was not followed.

The quantitive data obtained in this way from gamma-ray spectroscopy were then normalized as a result of the neutron flux monitoring (described later) and were corrected for the chemical yield of the radiochemical separations used. The amount of the desired element present in the sample was then determined from calibration curves obtained with standard amounts of the element.

Radiochemical separations and procedures

Each type of sample presents its own peculiar problems of separation. Fortunately there are now available monographs (National Research Council 1960) on the radiochemistry of individual elements which can be used as the starting point for individual procedures. Seldom, however, will it be possible to use a procedure given in the monographs without modification. Instead, procedures can be developed from information contained in the monographs in the same way the procedures below have been developed.

Monographs are now available for the elements studied in this paper: vanadium (Brownlee 1960), arsenic (Beard 1960), molybdenum (Scadden and Ballou 1960), tungsten (Mullins and Leddicotte 1961), rhenium (Leddicotte 1961), and gold (Emery and Leddicotte 1961). Additional information on the procedures developed for this study is also available (Meinke 1957, 1958).

1. *Vanadium.* In preliminary experiments the extraction of vanadium with TTA (thenoyltrifluoroacetone)-benzene and with cupferron (ammonium nitrosophenylhydroxylamine)-chloroform solutions was checked by using 3.8-min V^{52} as a tracer. For TTA extraction the vanadium gave good selectivity but required reduction to V^{+4} and showed the pH dependence of Figure 1. For a 1-min contact this extraction gave a yield of around 65% in a procedure requiring a total time of 5 min including the dissolution and reduction steps.

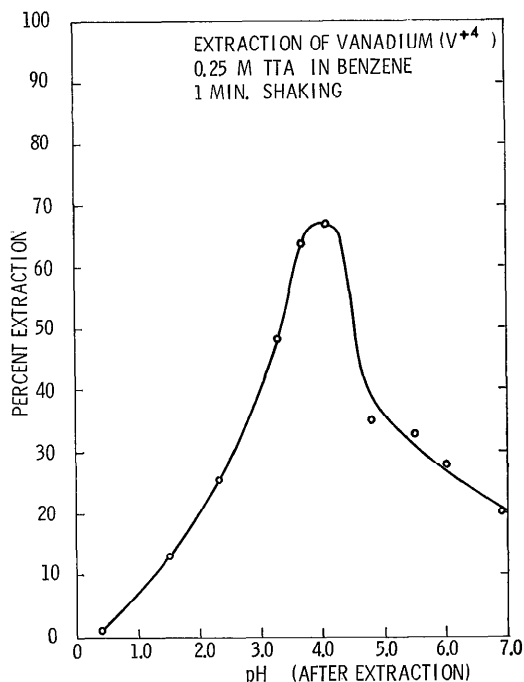Extraction of vanadium with cupferron-chloroform on the other hand gave recover-

FIG. 1.   Extraction of vanadium with TTA.

ies of about 90% in about 3 min including dissolution of the sample and required no reduction. Since time is important in working with the short-lived vanadium isotope, schemes including the cupferron extraction were adopted in the analyses of these samples, although this extraction is not as selective for vanadium as the TTA procedure.

Fifty to 100 mg of the ash sample were irradiated for 10 min in the pneumatic tube system of the reactor. The irradiated ash was digested for 30 sec in 15 ml of hot 4 M NaOH solution containing 10 mg of V^{+5} carrier. Next 10 ml of concentrated HCl were added to dissolve the residue and the solution was diluted to 50 ml with water.

The solution was transferred to a separatory funnel in which 10 ml of chloroform had already been placed. Then, 2.5 ml of 6% aqueous cupferron solution were added, the contents shaken vigorously for 30 sec, and allowed to stand for 40–60 sec to separate the layers.

The organic layer was then divided between two counting tubes. Gross gamma-ray decay was followed with one tube on

a scintillation well counter ($1 \times 1\frac{1}{2}$-in. crystal) while radiochemical purity was checked with the 100-channel gamma-ray spectrometer (3×3-in. crystal) in the energy range of 0–2 Mev. The decay of V^{52} (3.8-min half-life) was followed for about 20 min by both of the instruments.

The time required for the entire separation procedure was about 4 min and the chemical yield of the separation was around 90%. Radiochemical yields could be determined by subsequent precipitation of the vanadium cupferrate and weighing. However, the yield values were quite reproducible and were incorporated into the calibration curve as explained below.

2. *Arsenic.* Although distillation should be the best method for the radiochemical separation of arsenic, it requires time and some skill for successful operation. In the present work a simple chemical separation of arsenic by co-precipitation with phosphomolybdate has proven satisfactory when coupled with gamma-ray spectroscopy.

Three to 6 samples and standards were simultaneously irradiated in the reactor pool for 5–9 hr at the face of the reactor core. Each sample (~ 500 mg) was contained either in sealed quartz or polyethylene tubing of 8-mm diameter. The polyethylene tubing was preferable for irradiations of several hours duration at a power level of 100 kw because it minimized container radiation hazard in handling; however, it would fall apart under such irradiations at the full reactor power of 1,000 kw. The sealed samples and standards were placed together in a polyethylene container with lead shot as weight.

After irradiation, the samples were allowed to stand for 15 hr to eliminate short-lived activities, although considerable activity of Na^{24} and P^{32} still remained at the end of this cooling period. The irradiated ash was then dissolved in 5 ml of concentrated HNO_3 by heating. Ten milligrams of phosphorus carrier in phosphate solution were added and the solution diluted to 50 ml with water.
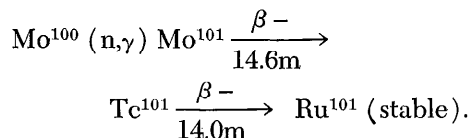
One milliliter of saturated bromine water was added to oxidize the As^{+3} to As^{+5} and

the excess Br_2 expelled by boiling. The solution was then heated. While hot, 3 g of NH_4NO_3 crystals and then 10 ml of 10% ammonium molybdate solution were added (temperature of the solution should be higher than 70°C) to precipitate the phosphomolybdate. The precipitate was allowed to stand for 20 min to settle and then was filtered and mounted for counting.

The 0.56-Mev gamma-ray of As^{76} along with a fairly high beta-ray activity of P^{32} was found on measurement with the 100-channel analyzer.

The time required for the whole separation procedure was about 30 min and the chemical yield about 60%. The chemical yield was determined by using tracer As^{76} in independent runs.

3. *Molybdenum.* The activation analysis of molybdenum by means of gamma-ray spectroscopy has been accomplished by using the short-lived Tc^{101} daughter activity produced as follows:

$$\text{Mo}^{100} \, (\text{n}, \gamma) \, \text{Mo}^{101} \xrightarrow[\;14.6\text{m}\;]{\beta -}$$

$$\text{Tc}^{101} \xrightarrow[\;14.0\text{m}\;]{\beta -} \text{Ru}^{101} \, (\text{stable}).$$

The per cent abundance of Mo^{100} is 9.62% and the thermal neutron cross section is 0.5 barns. By separating Tc^{101} from other isotopes and counting the Tc^{101} activity, the amount of molybdenum originally present can be estimated. For measuring this decay chain the radiochemical separation of technetium with tetraphenyl arsonium chloride as a complexing agent seems to be more specific than any separation procedure for molybdenum. In addition to this, the time required for dissolving the samples is not so critical if the Tc^{101} activity is counted instead of the Mo^{101} activity, since the Tc^{101} activity increases until 15 min after the end of the irradiation. Figure 2 shows an example of a spectrum of irradiated molybdenum, in which gamma-ray peaks of both Mo^{101} (0.191 Mev) and Tc^{101} (0.307 Mev) appear side by side. Figure 3 illustrates the decay of the Mo^{101} peak and the growth and decay of the Tc^{101} peak appearing in Figure 2.
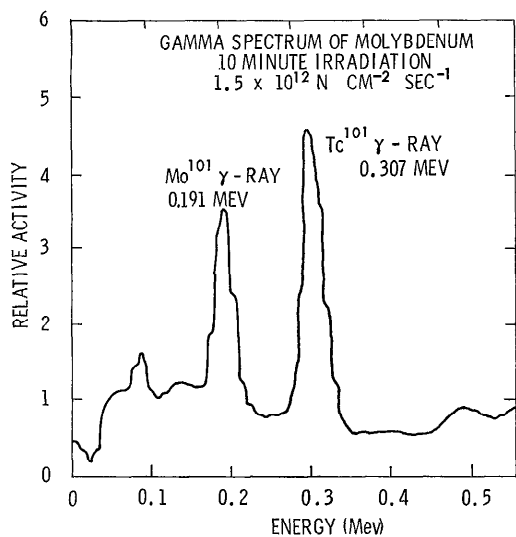
FIG. 2. Gamma-ray spectrum of Mo[101] and Tc[101].

FIG. 3. Growth and decay of Tc[101] gamma-ray peak.

A sample of 200–250 mg of the ash was sealed in polyethylene envelopes and irradiated for 15 min in the pneumatic tube. The irradiated ash was digested in a beaker with 3 ml of hot 12 M NaOH solution for 1 min and then 10 ml of concentrated HCl added to the solution. After the addition of 5 mg of rhenium carrier and 5 ml of saturated bromine water, the solution was allowed to stand for about 15 min to allow for growth of the Tc[101]. During this time the solution was kept warm.

Fifteen minutes from the end of the irradiation, the excess Br$_2$ was expelled by boiling without too much bubbling. A watch glass was put on the beaker as a cover, and 7 g of solid NaHCO$_3$ were added with care to avoid spattering. The solution was diluted to 30 ml with water and the pH adjusted to about 8 with a few drops of 4 M NaOH solution.

The solution was then transferred to a separatory funnel, 2 ml of 1% tetraphenyl arsonium chloride solution were added and the contents agitated for 1 min. Twenty ml of chloroform were added to the funnel and the contents shaken vigorously for 2 min. The organic layer was transferred to a beaker, 20 ml of 1 M HCl added, and the
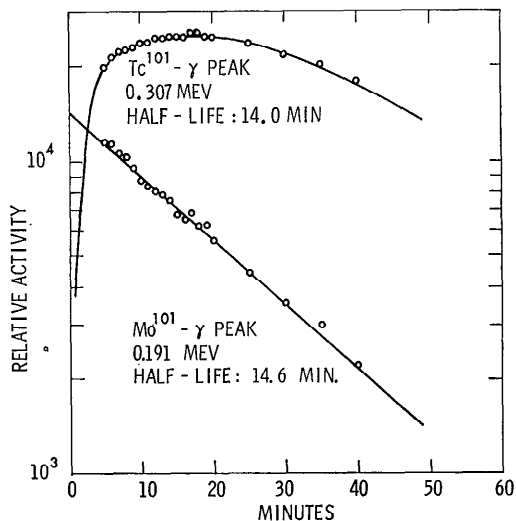
beaker placed on a hot plate to boil off the chloroform layer. This took about 3 min.

Two milliliters of bromine water were again added to make sure of the oxidation state and the excess Br$_2$ expelled by heating. While hot, 2 ml of tetraphenyl arsonium chloride solution were added. The solution was cooled by pouring liquid nitrogen directly on the surface of the solution. A temperature below 10°C should be obtained. The precipitate formed was filtered, washed twice with 3 ml of ice-cold water, and then mounted for counting.

The separated technetium activity was measured by gamma-ray spectrometry in the energy range of 0–1 Mev. The decay of the Tc[101] gamma-ray peak was followed for 10 min by recycling the counting every 1 min. The counts for every minute obtained under the Tc[101] photopeak were plotted against time on semi-logarithmic graphs and the activity at 15 min from the end of the irradiation was estimated by extrapolating back the straight line. By comparing the activity thus obtained with those for molybdenum standards processed under the same conditions, the molybdenum content of the samples was estimated.

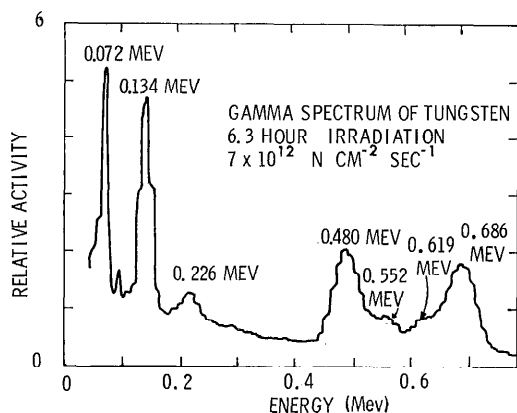The time required for the entire separation procedure was about 30 min including

FIG. 4. Gamma-ray spectrum of tungsten.

the waiting period of about 15 min. The chemical yield of the separation was about 60%. The chemical yield was determined in independent runs by using irradiated molybdenum. The standards were prepared in a manner similar to that of tungsten described in the next section.

4. *Tungsten.* For the activation analysis of tungsten, W^{187}, an isotope with a half-life of 24 hr and 7 characteristic gamma-rays within the energy range from 0–0.7 Mev was used. These 7 gamma-rays are shown in Figure 4 in a spectrum taken on irradiated tungsten. The 0.072-Mev gamma-ray was usually used for the quantitative determination of tungsten.

About 500 mg of the ash samples along with standard samples were sealed in polyethylene envelopes. The standards were prepared by drying known volumes (10–30 lambda) of tungsten standard solution on a small-sized filter paper of the best quality (15-mm diameter). The sealed samples and standards were then placed together in an aluminum can having a wall thickness of half an inch. The can was then inserted into the first row of the reactor core (in pool) and irradiated for 6.3 hr.

After a cooling period of 48 hr, the irradiated ash was digested in a beaker with 5 ml of hot 12 M NaOH solution to which 10 mg of tungsten carrier had been added. Ten milliliters of concentrated HCl were added and the solution made about 2 M in HCl by

dilution with water to 30 ml. After adding 0.2 g of solid $SnCl_2 \cdot 2H_2O$ and 0.5 g of solid NH_4SCN, the solution was heated for about 5 min to form the bright green complex.

The solution was transferred to a separatory funnel and extracted twice by shaking for 1 min with 30 ml portions of ethyl acetate. The organic layer was transferred to a large beaker and evaporated to dryness on a hot plate. The residue was then taken up in 10 ml of 6 M HCl. Five drops of 30% H_2O_2 and 0.5 ml of concentrated HNO_3 were added to the solution which was evaporated almost to dryness. Ten ml of 6 M HCl were again added and the solution stirred vigorously.

The yellow precipitate (WO_3) remaining was filtered, washed twice with 3 ml of 6 M HCl, and mounted for counting. The separated tungsten sample was measured on the gamma-ray spectrometer using the 0–0.25-Mev energy range and the spectra obtained analyzed for the 0.072-Mev gamma-ray of W^{187}. To make sure of the identification of W^{187}, the decay of this gamma-ray peak was followed for 3 days or more.

The time required for the entire separation procedure was about 40 min and the chemical yield was about 30%. Although this yield was not good when compared with other separation procedures used in the present work, a clean separation could be made. The chemical yield was determined by using irradiated tungsten standards in independent runs as well as by weighing the separated WO_3.

5. *Rhenium.* Rhenium has two stable isotopes: Re^{185} (37.08%) and Re^{187} (62.93%). By thermal neutron capture, three radioisotopes, which might be suitable for activation analysis are produced. These are: Re^{186} : half-life, 88.9 hr;

primary gamma-ray energy, 0.137 Mev. Re^{188} : half-life, 16.7 hr;

primary gamma-ray energy, 0.155 Mev. Re^{188m}: half-life, ~ 20 min;

primary gamma-ray energy, 63.5 Kev. In the present work, the 0.137-Mev gamma-ray peak of Re^{186} was used for spectroscopy.

At the same time, the possibility of utilizing Re[188m] has been considered.

About 500 mg of the ash samples and standards (prepared on filter paper in a manner similar to the tungsten determinations) were sealed in aluminum envelopes and placed in an aluminum can having a wall thickness of 0.5 in. The can was irradiated in the first row of the reactor core for 11.5 hr. The samples were then "cooled" for about 6 days before the chemical procedures were carried out. The samples were opened in an enclosed box shielded with 2 in. of lead. At the time of opening the samples, dose rates of 100–500 mr/hr for beta radiation and about 3 mr/hr for gamma radiation were encountered for each sample.

The irradiated ash was dissolved by heating a beaker containing 10 ml of concentrated HCl, 5 ml of saturated bromine water, and 5 mg of rhenium carrier. After the dissolution, the excess Br_2 was expelled by boiling. There is a distinct possibility of losing some of the rhenium when using bromine water in acid medium, so that the boiling should not be allowed to become too vigorous. The procedure continues as for the molybdenum determination above except that after the addition of liquid nitrogen, the solution was allowed to stand for 15 min to complete the precipitation.

The separated rhenium was measured with the gamma-ray spectrometer in the energy range of 0–0.5 Mev. The rhenium assay was made using the 0.137 gamma ray of Re[186]. The decay of this peak was followed for about a week to identify the Re[186].

The time required for the entire separation procedure was about 30 min and the chemical yield would run up to 70%. The chemical yield was determined by using irradiated rhenium standards in independent runs as well as by weighing the separated rhenium as tetraphenyl arsonium perrhenate, $(C_6H_5)_4AsReO_4$.

6. *Gold.* In order to develop procedures for the radio chemical separation of gold, the following steps were checked by using Au[198] tracer: extraction of gold from 6 M aqua regia solution with ethyl acetate; back-extraction of gold from the ethyl acetate layer with ammonium hydroxide; and precipitation of Au metal from 1 M HCl solution by reduction with SO_2 gas. Recoveries of more than 95% were obtained for each of the steps.

About 500 mg of the ash samples and the standard prepared on filter paper in a manner similar to those for the tungsten determination were sealed in polyethylene tubing and covered by 5 mil. of aluminum foil for protection. The sealed samples and standards were then put together in a polyethylene container with lead metal as weight and irradiated in the reactor core for 14.1 hr.

After cooling for about 5 days, the samples were opened in a lead shielded box. The irradiated ash was dissolved by heating in 15 ml of aqua regia, 10 mg of Au carrier added and the solution diluted to 30 ml with water.

The solution was then shaken for 2 min with 30 ml of ethyl acetate in a separatory funnel. The organic layer was washed by shaking for 1 min with 15 ml of 6 M HCl. The aqueous layer was discarded. The gold in the organic layer was stripped by shaking for 2 min with 25 ml of 2 M NH_4OH. The basic aqueous layer was then acidified in a beaker with 10 ml of concentrated HCl, heated, and SO_2 gas bubbled (3–5 bubbles/sec) through for 15 min to precipitate metallic gold. This gold was then filtered, washed twice with cold 1 M HCl, and mounted for counting.

The separated gold was measured by gamma-ray spectroscopy in the energy range of 0–1.0 Mev. The area under the 0.41 Mev gamma-ray peak of Au[198] was used for quantitative work. Decay of the Au[198] gamma-ray peak was followed for about a week to confirm the presence of gold.

The time required for the entire separation procedure was about 30 min and the chemical yield of the separation was about 80% or more. The chemical yield was determined on standard gold solutions by using Au[198] as a tracer, as well as by

FIG. 5. Calibration curve for vanadium in biological ash. Calcium oxide was used as matrix material for these standards.
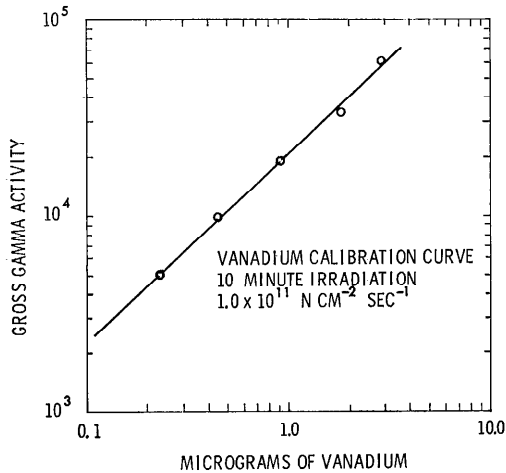

FIG. 6. Calibration curve for arsenic in biological ash. Calcium oxide was used as matrix material for these standards.

weighing the deposited gold resulting from the separation.

Flux monitoring and calibration curves

From measurements with flux monitors, the thermal neutron flux available in the pneumatic tube irradiations was found to be about 1×10^{12} neutrons cm^{-2} sec^{-1} at the operating power level of 1,000 kw. In the case of pool irradiations at 1,000 kw operation, a flux between 1 and 4×10^{12} neutrons cm^{-2} sec^{-1} was found depending on the locations on the side of the reactor core and also on the configuration of the reactor fuel elements. Operation at the 100-kw level reduced these fluxes by a factor of 10.

1. *Vanadium.* About 10 mg of gold foil was used for each irradiation as a flux monitor. After irradiation these gold foils were dissolved in 4 ml of aqua regia and diluted to 10 ml. A 100-lambda aliquot of this solution was then taken for counting.

For more than 20 irradiations an averaged flux of 0.89×10^{10} neutrons cm^{-2} sec^{-1} was obtained. The fluctuations in flux from one sample to another (and one day to another) at the nominal 100-kw level did not frequently exceed 10%.

A calibration curve shown in Figure 5 was compiled from data obtained for standard synthetic samples prepared by adding known amounts of vanadium to pure cal-
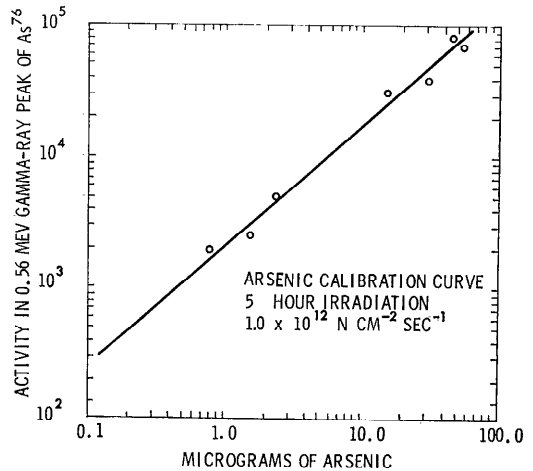
cium oxide. The range of the standards was from 0.23 to 2.7 μg of vanadium. The points plotted in the figure have been normalized to 10-min irradiation at a thermal neutron flux of 1.0×10^{11} neutrons cm^{-2} sec^{-1}. Correction for the chemical yield was not made on these points.

2. *Arsenic.* About 10-mg foils of aluminum-cobalt containing 0.546% cobalt were used for monitoring the neutron flux. After the short-lived (2.3 min and 10.7 min respectively) activity of aluminum and cobalt had died out, the long-lived (5.2 year) activity of Co^{60} was counted directly on the gamma-ray spectrometer. On the average, a flux of 6.1×10^{11} neutrons cm^{-2} sec^{-1} was obtained for these pool irradiations. However, fluctuations of the flux around this value were rather large depending upon the section of the surface of the core at which the samples were placed.

A calibration curve for the arsenic determination is given in Figure 6. This was based on the data obtained for standard synthetic samples prepared in a similar manner to those for vanadium. The range of the standards was from 0.77 to 50.6 μg of arsenic. The points plotted in the figure have been normalized to a condition of 5 hr irradiation at a thermal neutron flux of 1.0×10^{12} neutrons cm^{-2} sec^{-1}. Correction
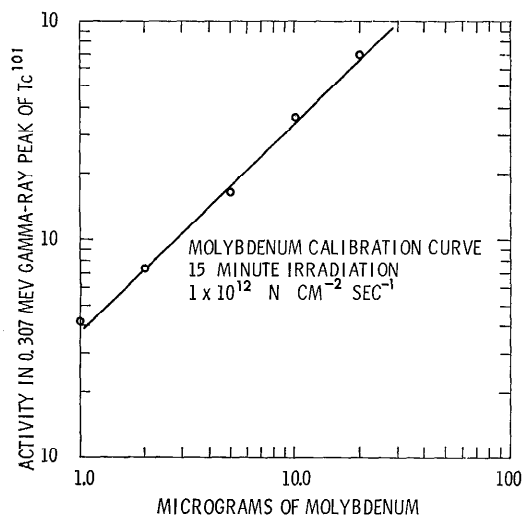
FIG. 7. Calibration curve for molybdenum in biological ash. Calcium oxide was used as matrix material for these standards.

FIG. 8. Calibration curve for tungsten in biological ash. Calcium oxide was used as matrix material for these standards.

for decay of As^{76} is included in the normalization, but no correction for chemical yield was made.

3. *Molybdenum.* Gold foils of about 1 mg were used as flux monitors. The treatment of the foil was similar to that of vanadium above. The average flux for 13 irradiations was 9.4×10^{11} neutrons cm^{-2} sec^{-1}.

The calibration curve for the determination of molybdenum is shown in Figure 7. The points plotted in the figure were obtained for standards ranging from 1.0 to 20 μg of molybdenum by normalizing the activity to 15 min irradiation at a flux of 1×10^{12} neutrons cm^{-2} sec^{-1}. Corrections for chemical yield were not included.

4. *Tungsten.* Aluminum-cobalt foils of about 5 mg containing 0.356% cobalt were used for flux monitoring. The average flux for these pool irradiations was 1.52×10^{12} neutrons cm^{-2} sec^{-1}.

From the counting data for the standards and the data of the flux monitoring, activities normalized to 10 hr irradiation at a neutron flux of 1×10^{12} neutrons cm^{-2} sec^{-1} were computed and plotted *versus* tungsten content as in Figure 8. The range of the standards was from 0.05 to 1.0 μg of tungsten. Corrections for decay and chemi-
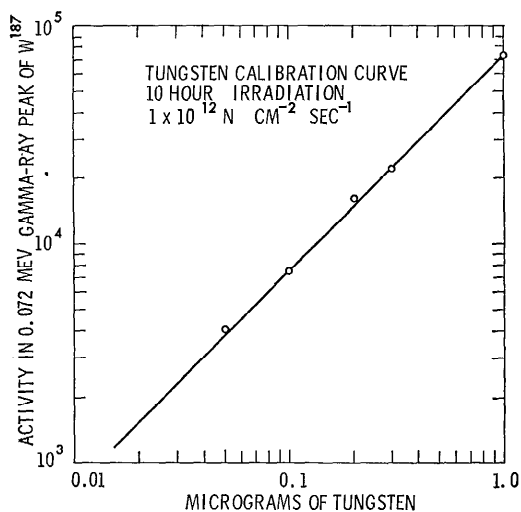
cal yield were included in the computations.

5. *Rhenium.* Aluminum-cobalt foils of about 5 mg containing 0.356% cobalt were used for the flux monitoring. An average flux of 3.5×10^{12} neutrons cm^{-2} sec^{-1} was obtained.

From the counting data for the standards and the data of the flux monitoring, activities normalized to 10 hr irradiation at a neutron flux of 1×10^{12} neutrons cm^{-2} sec^{-1} were computed and plotted *versus* rhenium content as in Figure 9. The range of the standards was from 0.001 to 0.06 μg of rhenium. Corrections for decay and chemical yield were included in the computations.

6. *Gold.* Aluminum-cobalt foils of 5–10 mg containing 0.356% cobalt were used for the flux monitoring. From the counting data of Co^{60} activity, an average thermal neutron flux of 2.5×10^{12} neutrons cm^{-2} sec^{-1} was obtained.

The calibration curve given in Figure 10 was compiled from counting data obtained for standards ranging from 0.007 to 0.24 μg of gold after chemical separations similar to those made on the samples. Activities plotted in the figure have been normalized to 10 hr irradiation at a thermal neutron
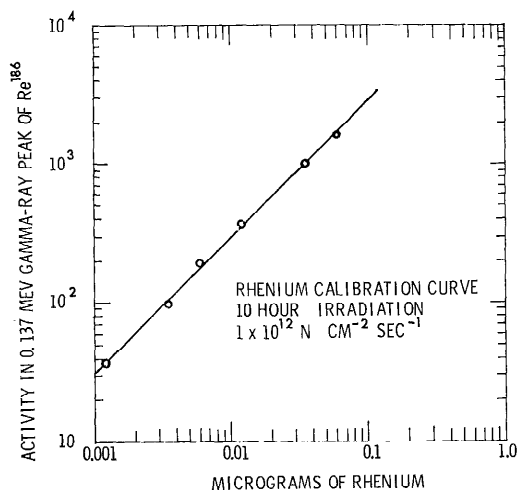
FIG. 9. Calibration curve for rhenium in biological ash. Calcium oxide was used as matrix material for these standards.
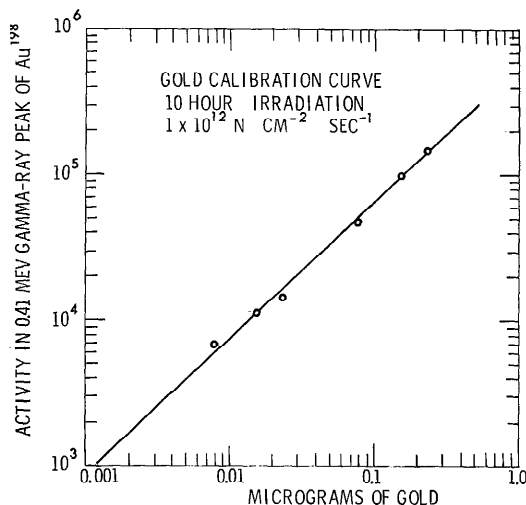

FIG. 10. Calibration curve for gold in biological ash. Calcium oxide was used as matrix material for these standards.

flux 1×10^{12} neutrons cm^{-2} sec^{-1}. Corrections for decay and chemical yield have been included.

RESULTS AND DISCUSSION

Experimental sensitivity

Sensitivities at flux levels of 10^{12} neutrons cm^{-2} sec^{-1} for each of the 6 elements dealt with in the present paper have been determined for the conditions of our experiments. In Table 3 these normalized experimental sensitivities are compared with those calculated for beta measurement for about the same condition by Schindewolf (1958). He assumed 10 hr or saturation irradiations at a neutron flux of 1×10^{12} neutrons cm^{-2} sec^{-1} and included the counting efficiencies for the Geiger counters used for the measurements of the radioisotopes in question. Since he used gross beta-ray counting rather than gamma-ray spectroscopy and did not include a cooling period or consider loss by chemical separation, it would be expected that the experimental (or practical) sensitivities might be poorer than those calculated. The higher sensitivity obtained for gold is discussed below. Table 3 also summarizes the mode of chemical separation and the chemical yield pertinent to each determination.

The sensitivities listed in this table are probably good to within a factor of 2 and are given only as an indication of the approximate limitations of the specific methods used. This is not to imply, however, that higher sensitivities are not possible with additional improvements in the methods. With higher neutron fluxes, the sensitivities are of course proportionately higher. Comments on the sensitivities reported for individual elements are summarized below.

1. *Vanadium.* In these analyses the gamma-ray spectra were used only to make a positive identification of vanadium by the characteristic 1.44-Mev gamma-ray peak. The quantitative data were based on the analysis of gross gamma-ray decay curves obtained with a scintillation well counter. The lower limit of quantitative determination by the scintillation well counter may be estimated to be as low as 0.02 μg V (10-min irradiation at a flux of 10^{11} neutrons cm^{-2} sec^{-1}) while because of geometry problems with the 3-in. crystal and the 100-channel analyzer, it is about 0.1 μg V. Reproducibility was fairly good since the probable error should not exceed $\pm$ 10%.

There are many possibilities for improving the procedure to increase the sensitivity.

TABLE 3. *Comparison of approximate experimental and calculated sensitivies[1]; mode of chemical separations*

Element	Vanadium	Arsenic	Molybdenum	Tungsten	Rhenium	Gold
Experimental sensitivity (g)* Flux: 1×10^{12} n cm^{-2} sec^{-1}	2×10^{-9}** (10 min irrad.)	5×10^{-8} (10 hr irrad.)	5×10^{-7} (15 min irrad.)	5×10^{-9} (10 hr irrad.)	1×10^{-9} (10 hr irrad.)	5×10^{-10} (10 hr irrad.)
Calculated sensitivity (g) Flux: 1×10^{12} n cm^{-2} sec^{-1} (Schindewolf 1958)	1.2×10^{-10} (satur.)	9×10^{-10} (10 hr irrad.)	3.2×10^{-8} (satur.)	1.2×10^{-9} (10 hr irrad.)	1×10^{-9} (10 hr irrad.)	3×10^{-10} (10 hr irrad.)
Mode of chemical separation	Cupferron–chloroform	Co–ppt. with phosphomolybdate	$(C_6H_5)_4$AsCl–chloroform	Thiocyanate–ethyl acetate	$(C_6H_5)_4$AsCl–chloroform	Ethyl acetate
Chemical yield	90%	~60%	60%	30%	70%	80%
Time required for the separation	~4 min	30 min	30 min†	40 min	30 min	30 min

[1] For exact experimental conditions, see text.
* This sensitivity includes a cooling period of one half-life for long-lived isotopes of arsenic, tungsten, rhenium, and gold, and correction for chemical yield.
** This value was estimated on the basis of counting with a gamma-scintillation well counter.
† This time includes a waiting period of 15 min.

However, since the sensitivity stated above seemed to be sufficient for the present samples, further improvements were not attempted.

2. *Arsenic.* In spite of the considerable Bremsstrahlung present in the sample from P^{32} beta rays, a definite gamma-ray peak of As^{76} was obtained in the gamma-ray spectra. The lower limit of quantitative determination at the normalized condition may be around 0.1 μg of arsenic (5-hr irradiation at a flux of 10^{12} neutrons cm^{-2} sec^{-1}) after the cooling period of one half-life. The probable error of the present analyses was around ± 25%, although the accuracy could be improved by more elaborate separation procedures.

3. *Molybdenum.* The lower limit of the quantitative determination at the normalized irradiation condition (15-min irradiation at a flux of 1×10^{12} neutrons cm^{-2} sec^{-1}) should be around 0.5 μg of molybdenum. The sensitivity may be increased somewhat by using the long-lived isotope of molybdenum (Mo^{99}: half-life, 66 hr) and longer irradiations, but the procedure would then become much more time-consuming.

The probable error expected for the analysis near this lower limit may be around ± 35%.

4. *Tungsten.* From the calibration curve and the chemical yield of the separation, the lower limit of the quantitative determination at the normalized condition (10 hr irradiation at a flux of 1×10^{12} neutrons cm^{-2} sec^{-1}) may be estimated to be around 5×10^{-9} g of tungsten after the cooling period of one half-life.

A probable error of between ± 40–50% may be expected for the values obtained near the lower limit of the determination. However, for the present determinations the errors should be within ± 30%.

5. *Rhenium.* From the calibration curve and the chemical yield of the separation, the lower limit of the quantitative determination at the normalized condition (10-hr irradiation at a flux of 1×10^{12} neutrons cm^{-2} sec^{-1}) may be estimated to be around 1×10^{-9} g of rhenium after the cooling period of one half-life and the chemical separation.

The probable error for the determination of rhenium near the lower limit may be around ± 35%. The errors included in the present analyses should be less than ± 25%.

6. *Gold.* In the course of the calibration more activity was obtained for a given amount of gold in the standards than was expected. This fact may possibly be inter-
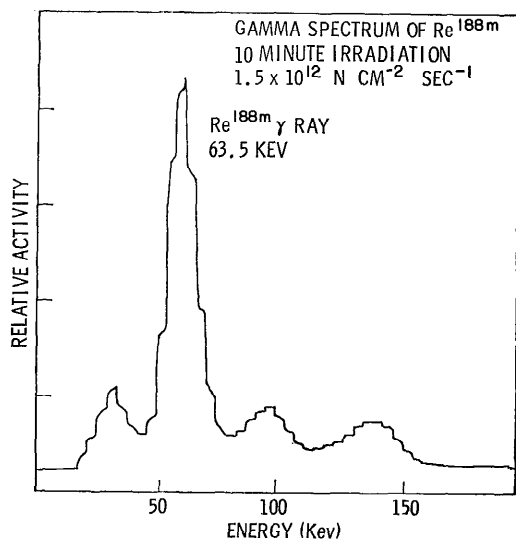
FIG. 11.   Gamma-ray spectrum of 63.5-kev gamma-ray peak of Re^{188m}.

FIG. 12.   Decay curve of Re^{188m}.

preted by the resonance effect of fast neutrons from the reactor in the formation of Au^{198}. The lower limit of the quantitative determination at the normalized condition (10-hr irradiation at a neutron flux of 1×10^{12} neutrons cm^{-2} sec^{-1}) may be estimated to be around 5×10^{-10} g of gold after a cooling period of one half-life and the chemical separation stated above.

The probable error of the analysis near the lower limit of the determination may be around $\pm$ 50%. The error of the analyses performed here should be $\pm$ 30% or less.

Notes on the short-lived isotope of rhenium

The possibility of utilizing the short-lived rhenium isotope, Re^{188m}, in activation analysis seems promising. Figures 11 and 12 show respectively the 63.5-kev gamma-ray peak of Re ^{188m} and its decay. A half-life of 20.6 min was obtained in the present experiment which does not agree with the values of 18.7 min (Flammersfeld 1953) and 22 min (Mihelich 1953) reported to date. At any rate, since the utilization of the short-lived rhenium isotope for activation analysis should decrease the formation of the contaminating activities (Na^{24} and P^{32}) induced in the samples, the chemical separation procedures may be carried out much
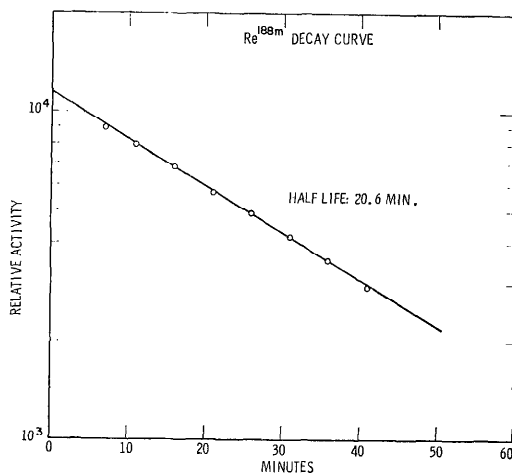
more easily than when using the long-lived isotope. The lower limit for the determination of rhenium by using Re^{188m} should be around 1×10^{-8} g of rhenium for a 10-min irradiation at a neutron flux of 1×10^{12} neutrons cm^{-2} sec^{-1} and including chemical yield.

Results obtained

The results obtained for the abundance in marine biological samples of the 6 trace elements dealt with in the present work are given in Table 4. The overall errors accompanying these values should rarely exceed $\pm$ 30%. Since the numbers of the organisms analyzed were quite small, it is difficult to deduce definite conclusions from these values. However, they are valuable as a complement to the information summarized in Table 1 and the general review of Fukai and Meinke (1959a). A general tendency towards decreasing abundance with the higher trophic level may be suggested.

SUMMARY

Activation analysis deserves much wider consideration in the field of oceanography than it has received to date. Although a nuclear reactor is required for high sensitivity analyses by this method, many elements possess radioisotopes of sufficiently long half-life so that service irradiations at commercial reactor facilities can be utilized. The necessary purification and monitoring

TABLE 4. *Abundance of trace elements in Marine Biological Ash*

Element	Vanadium		Arsenic		Molybdenum		Tungsten		Rhenium		Gold	
Basis	g/g ash	g/g dry matter	g/g ash	g/g dry matter	g/g ash	g/g dry matter	g/g ash	g/g dry matter	g/g ash	g/g dry matter	g/g ash	g/g dry matter
Ulva sp. (seaweed) collected at Enoshima, Sagami Bay, Japan in May 1956	5.9×10^{-6}	1.3×10^{-6}	5.4×10^{-6}	1.2×10^{-6}	*	*	1.3×10^{-7}	2.9×10^{-8}	7.3×10^{-8}	1.6×10^{-8}	9.3×10^{-8}	2.1×10^{-8}
Ulva sp. (seaweed) collected at Urayasu, Tokyo Bay, Japan in May 1956	1.33×10^{-5}	3.1×10^{-6}	—	—	*	*	1.8×10^{-7}	4.2×10^{-8}	4.6×10^{-8}	1.1×10^{-8}	1.5×10^{-8}	3.5×10^{-9}
Porphyra sp. (seaweed) collected at Chiba, Tokyo Bay, Japan in January 1957	2.12×10^{-4}	1.6×10^{-5}	—	—	1.7×10^{-5}	1.0×10^{-6}	—	—	—	—	—	—
Tapes japonica (little-neck clam) (mollusk; soft parts) collected on the shore of Japan Isles in 1958	1.50×10^{-5}	1.1×10^{-6}	$<5 \times 10^{-8}$	$<3.6 \times 10^{-9}$	—	—	4.6×10^{-7}	3.3×10^{-8}	6.4×10^{-8}	4.6×10^{-9}	7.9×10^{-8}	5.7×10^{-9}
Pandalus sp. (prawn) (crustacean, soft parts) collected in the vicinity of Japan Isles in 1958	1.1×10^{-6}	6.8×10^{-8}	8.3×10^{-7}	5.1×10^{-8}	—	—	$<5 \times 10^{-9}$	$<3.1 \times 10^{-10}$	$<5 \times 10^{-9}$	$<3.1 \times 10^{-10}$	4.6×10^{-9}	2.8×10^{-10}
Pneumatophorus japonicus (mackerel) (fish, muscle) collected in the vicinity of Japan Isles in 1958	*	*	3.4×10^{-7}	1.5×10^{-8}	—	—	$<1.4 \times 10^{-8}$	$<6.3 \times 10^{-10}$	$<8 \times 10^{-9}$	$<3.6 \times 10^{-10}$	2.6×10^{-9}	1.2×10^{-10}

* Below detection limit. The notation $<$ indicates that some uncertainty was included in identification of the elements by gamma-spectroscopy.

procedures can be developed without too much difficulty from the voluminous radio-chemical literature.

In comparison with other techniques of trace analysis, activation analysis gives considerably higher sensitivity for many elements and, of even more importance, eliminates the problems of reagent contamination and reagent blanks.

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