

# Trace Analysis of Marine Organisms: A Comparison of Activation Analysis and Conventional Methods<sup>1</sup>

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## ABSTRACT

A comprehensive review has been made of the abundance values reported for all trace elements in seaweed, mollusks, crustaceans, fishes, and in sea water. The sensitivities of standard spectrophotometric and flame photometric techniques for such analyses have been compared with the sensitivities expected from activation analysis techniques.

Activation analysis eliminates the problem of contamination by reagents and is particularly useful for the analysis of minute traces. While it is not an "all purpose" method for every element, it does show promise of increasing the detection sensitivity for a number of elements by factors of 10, 100, or more as well as making possible the discovery of elements not previously found in marine organisms, such as elements of the ruthenium or platinum groups and indium.

## INTRODUCTION

Studies of trace elements in biological materials were initially made by spectrographic analysis, augmented more recently by flame photometry. Concentration of these elements has been aided by solvent extraction with organic reagents and by ion-exchange. Nevertheless, the systematic knowledge of the abundance of trace elements in marine organisms is far from complete.

The most serious difficulty encountered in such analyses is contamination by minute quantities of the desired element which are present in the reagents used. The reliability of the results thereby tends to be lowered, even when carefully determined "reagent blank" values are subtracted.

The technique of radioactivation analysis is not limited by this consideration, since only the trace elements in the sample are activated (and subsequently measured). In activation analysis the constituents of a sample are determined by utilizing certain nuclear properties of the isotopes of the elements in the sample. Radioactive isotopes are formed by activation of the nuclei

of the sample elements using nuclear particles. These radioisotopes formed can then be detected and measured by their nuclear radiations. Thus a knowledge of their nuclear characteristics allows a determination of the amount of element present.

This technique has been used for determination of submicrogram amounts of elements in semi-conductors (Jakovlev 1955, Smales 1955c), for measuring trace impurities in construction materials for nuclear reactors (Jenkins and Smales 1956), and in the field of geochemistry of minor elements (*e.g.*, Brown and Goldberg 1949, Goldberg and Brown 1950, Smales 1952, Smales 1955a, Smales and Salmon 1955, Vincent and Smales 1956). It has also been applied to the analysis of trace elements in biological materials (Loveridge and Smales 1957). Several review articles covering various aspects of this technique have also been published (Jenkins and Smales 1956, Meinke 1956, Meinke 1958, Meinke and Maddock 1957, Smales 1955b).

It should be kept in mind, however, that activation analysis is not an "all purpose" method for any element in any type of sample. A general comparison (Meinke 1955) of the sensitivity of activation method with that of other methods has already been made, in addition to more specific comparisons (Jenkins and Smales 1956, Schindewolf 1958). Such information should be valuable

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in determining which elements are suited to activation analysis in studies of trace elements in marine organisms.

In the present phase of this study it is important not only to describe the occurrence of elements in samples, but also to deduce the laws governing the distributions and variations of these elements. Here the radioactivation technique should prove to be a powerful tool.

In the following sections, a review of current values of the abundance of trace elements in marine organisms will be given. Consideration of the sensitivity of activation analysis for these elements is also included.

#### ABUNDANCE OF TRACE ELEMENTS IN MARINE BIOLOGICAL MATERIALS AND SEA WATER

##### —LITERATURE SUMMARY

Table 1 gives the most reliable, up-to-date abundance values for trace elements in marine organisms and sea water, estimated on the basis of the data in the literature. Appropriately weighted data from two or more authors were cited when possible.

The four groups—seaweeds, mollusks, crustaceans, and fishes—were chosen as representatives of marine organisms, while sea water was added as the source of the elements contained in these marine organisms. It is admittedly sometimes difficult to obtain a representative value 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.

The significance of the table, therefore, is not to offer a basis for precise discussions, but only to generalize the abundance of trace elements in marine organisms preliminary to further detailed studies.

It is well known that the content of some elements in sea water varies considerably with the location of sample collection. For simplicity, values for the oceanic surface water have been given in the table. Although coastal waters should be the more important environment of organisms, variation in conditions makes it difficult to obtain representative values for these waters. It may be possible, however, to estimate an

order of magnitude of content of coastal waters from that of the oceanic water.

All trace elements that have been mentioned in the literature on marine organisms are included in the table. Eleven elements, including hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, phosphorus, sulfur, chlorine, potassium, and calcium have been excluded since they are major constituents of marine organisms. Lanthanide elements have been tabulated together since no reliable data on the separation and determination of each rare earth element have been reported.

Comments regarding each element included in Table 1 are given below. References on which these comments are based are listed in the table.

#### A. *Lithium to silicon*

Since elements that are primary components of biological materials were excluded, only six elements of this series remain.

Although at present only a few data have been reported for lithium, many more should be forthcoming since its sensitivity to the flame-photometric method is very high. Beryllium has been detected only qualitatively in the ash of seaweeds by spectrographic analysis.

Most of the data for fluorine are quite recent and show about equal concentrations in each group of organisms.

Despite the widespread occurrence of aluminum and silicon, reliable values for these elements are quite rare, probably because of easy contamination of the sample. Aluminum content tends to decrease with ascending trophic level.

#### B. *Scandium to zirconium*

These elements include most of the metals which appear to be important for the metabolism of marine organisms.

No direct determination of scandium has been made, although the estimated value for sea water has been given.

Titanium decreases with the ascending trophic level in a manner similar to aluminum, so that the ratio of aluminum to titanium remains constant in any group of

TABLE 1. Occurrence of trace elements in marine organisms and sea water

All references through 1957 are included. These are tabulated in columns labelled "Sources of data" by corresponding numbers in list of references. Figures in the columns pA are the negative logs of abundance (grams of element/grams dry weight at 105-110°C).

Atomic no.	Element	Seaweeds		Mollusks (without shell)		Crustaceans (without carapace)		Fishes (soft parts)		Sea water (in solution)	
		pA	Sources of data	pA	Sources of data	pA	Sources of data	pA	Sources of data	pA	Sources of data
3	Li	5.7	9, 12	6.0	27,111	—	—	+	109	7.0	103
4	Be	+	24, 58	—	—	—	—	—	—	—	—
5	B	3.8	31, 42, 53, 81	4.3	31,111	4.3	31,111	5.0	31	5.35	42,109
9	F	5.0	109	5.3	66, 105	5.3	66, 105	5.3	22, 66, 105, 109	5.85	13
13	Al	4.2	30, 71, 114	4.3	72	4.7	72	5.3	71, 109	8.5	45, 90
14	Si	3.0	30, 109	(3.0)	109	(2.5)	108	3.5	101	6.3	1, 29
21	Sc	(6.0)	4	—	—	—	—	—	—	(10.4)	34
22	Ti	4.5	12, 30, 36	4.7	11, 49	5.0	11, 49	5.7	80	9.0	36, 80
23	V	5.7	4, 8, 12, 109	6.0	6, 8, 51	6.3	6, 8	6.7	6, 8, 80	9.5	12, 43, 54, 60, 80, 110
24	Cr	6.0	4, 12, 114	—	—	+	78	6.7	78, 80	10.3	12, 43, 54, 80
25	Mn	4.3	12, 30, 81	4.5	109	4.5	109, 111	4.7	80, 85	9.5	32, 38
26	Fe	3.1	12, 30	3.5	79	4.3	26, 79	4.3	79	8.5	23, 61, 90
27	Co	6.3	4, 12, 64, 96	6.3	64, 106	6.7	64, 106	6.7	64, 80, 106	10.0	12, 32, 43, 54, 60, 80
28	Ni	5.7	4, 12, 64, 114	6.0	64	6.3	64	6.3	64, 80	9.5	12, 32, 43, 54, 60, 80
29	Cu	5.1	4, 12, 81	4.3	7, 65, 79	4.5	7, 26, 79, 109	5.3	7, 16, 79	9.0	2, 20, 74
30	Zn	4.3	4, 12, 114	(3.5)	84, 109	(3.3)	84, 109	4.0	80	8.5	54, 74
31	Ga	(6.3)	4, 24, 109	—	—	—	—	7.0	80	7.5	19, 80
32	Ge	+	24, 58, 109	—	—	—	—	6.0	80	7.3	19, 80
33	As	4.5	35, 89, 113, 114	5.4	89	5.3	89, 109	5.2	80, 89	8.5	35, 43, 97
34	Se	—	—	—	—	—	—	—	—	(8.4)	34, 43, 110
35	Br	3.2	50, 77	(3.5)	77, 109	(4.0)	109	(5.3)	77	4.2	103, 109
37	Rb	5.0	10, 15, 98	5.0	27	—	—	—	—	6.9	15, 44, 98
38	Sr	3.5	14, 17, 99	3.8	17, 111	(3.7)	14	3.8	111	5.1	17, 21, 41, 91
39	Y	±	109	—	—	—	—	—	—	(9.5)	34
40	Zr	(5.5)	4	—	—	—	—	—	—	+	109
41	Nb	—	—	—	—	—	—	±	78	—	—
42	Mo	6.3	4, 5, 12	5.7	7	6.3	7	6.3	7, 80	(9.3)	12, 43, 54, 60, 80, 110
47	Ag	6.5	4, 12, 114	+	27	+	27, 78	(5.0)	78, 80	9.7	12, 54, 80
48	Cd	6.2	63, 75	5.7	75, 104, 111	6.8	75, 104	(6.3)	80, 104	10.0	32, 54, 75, 80
50	Sn	6.0	4, 12, 114	(4.7)	111	(4.7)	111	5.5	80	8.5	12, 80
51	Sb	+	24, 58	—	—	—	—	6.7	80	>9.3	80
53	I	3.8	37	5.7	79	6.0	3, 26, 79, 109	5.7	79, 109	7.3	102, 103
55	Cs	7.0	98	—	—	—	—	—	—	9.3	44, 98
56	Ba	5.3	17	6.5	14, 17	(6.3)	111	+	78	8.2	17
57-71	Lanthanide Els.	+	4, 88	—	—	—	—	—	—	9.2	34
74	W	±	24, 58	—	—	—	—	—	—	10.0	43, 54
75	Re	±	46	—	—	—	—	—	—	—	—
79	Au	(6.0)	4, 24	—	—	—	—	8.0	80	10.5	40, 82
80	Hg	7.5	83	—	—	—	—	(6.5)	83	10.5	34, 54
81	Tl	—	—	—	—	—	—	—	—	>11.0	32, 80
82	Pb	5.3	4, 12, 114	5.7	73, 109	6.0	73	6.5	80	8.3	12, 32, 54, 80
83	Bi	+	24, 46	—	—	—	—	7.5	80	9.7	54, 80
88	Ra	13.3	25, 28, 56, 112	—	—	13.3	25, 56	13.7	56	16.2	39, 52
90	Th	(6.0)	4	—	—	—	—	—	—	13.4	39, 52
92	U	+	24, 58	—	—	—	—	—	—	8.7	52, 76, 100

+ element has only been detected.

— element has not been detected or reported.

± detection uncertain.

(□) less reliable values.

Figures in *italics* include results obtained by activation analysis.

organisms. However, the values used in the estimation of these representative values are somewhat dated.

Vanadium shows variations similar to aluminum and titanium. It is known, however, that this element is concentrated in certain species of mollusks. Since recent reported values for vanadium content in sea water seem to be high and since relatively large variations of vanadium content in coastal waters are likely to occur, the accumulation of more precise data is required.

Only a few values are available for chromium.

Although marine organisms contain a relatively large amount of manganese and iron, it was recently proven that the amount of these elements in true solution in sea water is extremely low and that they exist for the most part in particulate form (Goldberg 1954, Harvey 1949, Lewis and Goldberg 1954).

The fact that cobalt is concentrated relative to nickel in marine organisms is interesting, since Vitamin B<sub>12</sub> is a cobalt-containing compound. Content of these two elements shows considerable variation from species to species.

Only a few of the many data reported for copper and zinc can be considered reliable since the older methods used have been shown to give high results. It is well known that copper is concentrated in the blood of mollusks and crustaceans, while zinc appears more highly concentrated in marine animals than in seaweed.

Although new information for gallium and germanium in sea water is available, the values seem rather high when compared with previous values.

Analyses of arsenic have been made by several methods including the radioactivation method for sea water. Only a value estimated from the content in sedimentary rocks is available for selenium.

Although bromine is relatively abundant in marine organisms as well as in sea water, the wide spread of reported values indicates considerable uncertainty about this element.

Activation analysis data for rubidium and strontium in sea water and in some groups of marine organisms have recently been

published (Bowen 1956, Smales and Salmon 1955).

Reliable data are not available for yttrium and zirconium, although some values have been listed for purposes of reference.

### C. *Niobium to barium*

These elements range from atomic number 41 to 56. Only nine of these elements have been inserted in the table. In the future, however, activation analysis should provide a sensitive method for additional elements such as ruthenium, rhodium, palladium, and indium.

Reports on niobium are limited to a possible detection in some fish.

Many values have been published for molybdenum, especially for its abundance in sea water. Reexamination of these data might reconcile discrepancies among individual values.

Since the value obtained for silver in fishes appears too high and since the analyses were done near the lower limit of detection, rechecks of the values are desirable.

Reliable data from cadmium have been supplied recently. It is interesting that radioactive cadmium ( $Cd^{113m}$ ,  $Cd^{115m}$ ) was found in the soft tissues of some fishes caught near Bikini Atoll (Unpublished data from Tokai Regional Fisheries Research Lab., Tokyo, Japan). This fact may suggest some physiological significance of cadmium in the metabolism of marine organisms.

Since a definite tendency towards concentration of tin is implied from the values in the table, more measurements should be made in the future to verify this idea.

Only a few data have been reported for antimony.

Iodine is the only element for which comprehensive studies have been carried out. A number of data have been accumulated for the occurrence and variation of this element in marine organisms. It is known that the content of iodine varies greatly from species to species and, therefore, the value quoted for each group of organisms represents only an average abundance.

Recently, reliable activation analysis data for cesium and barium in sea water as well as in marine organisms have indicated that

the abundance of these elements is less by a factor of 10 than that previously accepted (Bowen 1956, Smales and Salmon 1955). As for cesium, comprehensive studies have been planned in connection with radio-cesium ( $Cs^{137}$ ) contamination from radioactive fall-out.

#### D. Lanthanum to uranium

There are relatively few data for these elements except for some rather out-of-date

values for lead and radium. The amount of gold and uranium in sea water has recently been determined by activation analysis. The gold content of coastal waters varies over a wide range.

It may be expected that data for the lanthanide elements will be supplied by application of the activation technique.

More work should be done on tungsten and rhenium.

TABLE 2. Comparison of sensitivities of activation method with those of conventional methods for the elements present in marine samples

Atomic No.	Element	Sensitivity of activation analysis				Sensitivity of conventional analysis		
		Mass No. of parent	Half-life of daughter	Sensitivity (g)	Sensitivity index	Sensitivity (g)	Sensitivity index	Method
21	Sc	45	<b>85d</b>	$3 \times 10^{-8}$	7.5	$4 \times 10^{-7}$	6.4	Morin
22	Ti	50	5.8m	$5 \times 10^{-6}$	5.3	$4 \times 10^{-6}$	5.4	Hydrogen peroxide
23	V	51	3.8m	$6 \times 10^{-8}$	7.2	$3 \times 10^{-7}$	6.5	Phosphotungstate
24	Cr	50	27d	$1 \times 10^{-5}$	5.0	$4 \times 10^{-7}$	6.4	Diphenylcarbazine
25	Mn	55	2.6h	$1 \times 10^{-10}$	10.0	$5 \times 10^{-6}$	5.3	Permanganate
26	Fe	58	45d	$1 \times 10^{-5}$	5.0	$1 \times 10^{-6}$	5.0	o-Phenanthroline
27	Co	59	<i>10.5m</i>	$2.5 \times 10^{-7}$	6.6	$5 \times 10^{-7}$	6.3	Nitroso-R salt
28	Ni	64	2.6h	$1 \times 10^{-7}$	7.0	$1 \times 10^{-5}$	5.0	Dimethylglyoxime
29	Cu	63	12.8h	$5 \times 10^{-9}$	8.3	$2 \times 10^{-6}$	5.7	Dithizone
30	Zn	68	<b>52m</b>	$1 \times 10^{-8}$	8.0	$2 \times 10^{-6}$	5.7	Dithizone
31	Ga	69, 71	21m, 14.1h	$5 \times 10^{-9}$	8.3	$1 \times 10^{-7}$	7.0	Fluorometric
32	Ge	74	82m	$1 \times 10^{-8}$	8.0	$1 \times 10^{-5}$	5.0	Heteropoly-molybdate
33	As*	75	26.6h	$2 \times 10^{-9}$	8.7	$5 \times 10^{-6}$	5.3	Heteropoly-molybdate
34	Se	80	18m	$3 \times 10^{-8}$	7.5			
35	Br	79	<i>4.5h, 18m</i>	$2 \times 10^{-9}$	8.7			
37	Rb*	85, 87	18.6d, 17.8m	$2.5 \times 10^{-7}$	6.6	$4 \times 10^{-7}$	6.4	Flame-photometric
38	Sr*	86	2.8h	$2 \times 10^{-7}$	6.7	$4 \times 10^{-7}$	6.4	Flame-photometric
39	Y	89	64.2h	$1.5 \times 10^{-8}$	7.8			
40	Zr	96	17h	$1 \times 10^{-6}$	6.0	$4 \times 10^{-5}$	4.4	Alizarin
41	Nb	93	6.6m	$2.5 \times 10^{-7}$	6.6	$2 \times 10^{-5}$	4.7	Quinalizarin
42	Mo	98, 100	67h, 14.6m	$2.5 \times 10^{-7}$	6.6	$2 \times 10^{-6}$	5.7	Thiocyanate-stannous chloride
47	Ag	107	2.3m	$1 \times 10^{-6}$	6.0	$1 \times 10^{-6}$	6.0	p-Dimethylaminobenzilidenerhodamine
48	Cd	116	2.9h	$3 \times 10^{-8}$	7.5	$1 \times 10^{-7}$	7.0	Dithizone
50	Sn	120, 122	27.5h, 4.0m	$5 \times 10^{-7}$	6.3	$2 \times 10^{-5}$	4.7	Dithiol
51	Sb	121	2.8d	$1 \times 10^{-8}$	8.0	$2 \times 10^{-6}$	5.7	Rodamine B
53	I	127	25m	$1 \times 10^{-9}$	9.0			
55	Cs*	133	<i>3.2h, 2.3y</i>	$5 \times 10^{-7}$	6.3	$4 \times 10^{-6}$	5.4	Flame-photometric
56	Ba*	138	85m	$8 \times 10^{-9}$	8.1	$1 \times 10^{-5}$	5.0	Flame-photometric
74	W	186	24h	$2.5 \times 10^{-9}$	8.6	$2 \times 10^{-7}$	6.7	Thiocyanate-reducing agent
75	Re	187	17h	$3 \times 10^{-10}$	9.5	$1 \times 10^{-6}$	6.0	Thiocyanate
79	Au*	197	2.7d	$6 \times 10^{-10}$	9.2	$2 \times 10^{-7}$	6.7	Rhodanine
80	Hg	196	65h	$\dagger 2 \times 10^{-8}$	7.7	$3 \times 10^{-5}$	4.5	Dithizone
81	Tl	203	3y	$7 \times 10^{-6}$	5.2	$2 \times 10^{-5}$	4.7	Iodine
82	Pb	208	3.3h	$2.5 \times 10^{-5}$	4.6	$2 \times 10^{-6}$	5.7	Dithizone
83	Bi	209	5d	$5 \times 10^{-6}$	5.3	$2 \times 10^{-6}$	5.7	Dithizone

\* Elements for which activation analysis methods have already been used.

† Sensitivity based on  $\gamma$ -counting with scintillation counter.

Half-lives in italics or boldface indicate those for metastable or ground state daughter, respectively.

TABLE 3. Comparison of sensitivities of radioactivation method with those of conventional methods for the elements unknown in marine samples

Atomic No.	Element	Sensitivity of radioactivation analysis				Sensitivity of conventional analysis		
		Mass No. of parent	Half-life of daughter	Sensitivity (g)	Sensitivity index	Sensitivity (g)	Sensitivity index	Method
44	Ru	104	4.5h	$2.5 \times 10^{-8}$	7.6	$1 \times 10^{-6}$	6.0	Thiourea
45	Rh	103	<i>4.4m</i>	$2.5 \times 10^{-8}$	7.6	$2 \times 10^{-6}$	5.7	Stannous chloride
46	Pd	108	13.6h	$2.5 \times 10^{-9}$	8.6	$5 \times 10^{-7}$	6.3	Nitrosophenylamino
49	In	115	54m	$2.5 \times 10^{-11}$	10.6	$2 \times 10^{-5}$	4.7	Dithizone
52	Te	126	9.4h	$5 \times 10^{-8}$	7.3			
72	Hf	180	46d	$3 \times 10^{-7}$	6.5			
73	Ta	181	<b>112d</b>	$1.5 \times 10^{-7}$	6.8			
76	Os	192	31.5h	$4 \times 10^{-8}$	7.4	$2 \times 10^{-5}$	4.7	Thiourea
77	Ir	193	19h	$2 \times 10^{-10}$	9.7	$2 \times 10^{-5}$	4.7	Chloroirdate
78	Pt	198	31m	$2 \times 10^{-8}$	7.7	$2 \times 10^{-5}$	4.7	Stannous chloride

Half-lives in italics or boldface indicate those for metastable or ground state daughter, respectively.

#### SENSITIVITY OF RADIOACTIVATION ANALYSIS FOR TRACE ELEMENTS

The term sensitivity is defined as the weight of an element that would produce a measurable amount of radioactivity after it had been irradiated by a given flux of neutrons for a given period of time.

As previously described (Meinke 1955) the general equation governing analysis by activation is

$$\text{Grams of X} = \frac{\text{Act.} \times \text{at. wt.}}{6.02 \times 10^{23} f(\sigma_{\text{at}}) 1 - e^{-\frac{0.693t}{t_{1/2}}}}$$

where Act. is the radioactivity (dis. sec.<sup>-1</sup>), at. wt. is the atomic weight of the isotope activated,  $f$  is the flux of neutrons (neutrons cm<sup>-2</sup> sec.<sup>-1</sup>),  $\sigma_{\text{at}}$  is the atomic cross section,  $t$  is the period of irradiation, and  $t_{1/2}$  is the half-life of the resultant radioisotope. Since at. wt.,  $\sigma_{\text{at}}$  and  $t_{1/2}$  are constants for a given isotope, we see that the weight detected is proportional to the activity, the flux, and the time of irradiation.

Consequently, if we choose a proper neutron flux and irradiation time and evaluate the activity so as to be the lower detection limit of a radioactivity measurement by suitable instruments, we determine the sensitivity of radioactivation analysis under ideal conditions. The sensitivity of the analysis can be improved by increasing the neutron flux, the irradiation time (for long-lived isotopes), and/or the sensitivity of the

instruments used for the radioactivity measurements.

Leddicotte and Reynolds (1953) computed the sensitivity of activation analysis for each element assuming a neutron flux of  $5 \times 10^{11}$  neutrons cm<sup>-2</sup> sec.<sup>-1</sup> and an irradiation period of ten half-lives or 30 days, whichever was shorter. Jenkins and Smales (1956) assumed a similar irradiation period in their computations, but they assumed a neutron flux of  $10^{12}$  neutrons cm<sup>-2</sup> sec.<sup>-1</sup>, introduced a time of two hours for the required radiochemical separation, and also considered the detector counting efficiencies for the  $\beta$ - or  $\gamma$ -emitting radioisotopes. Their irradiation period of 1 month, however, seems to be too long for a general analytical procedure.

Recently Schindewolf (1958) computed sensitivities based on a neutron flux of  $10^{12}$  neutrons cm<sup>-2</sup> sec.<sup>-1</sup> and irradiation times of 6 minutes and 600 minutes (10 hours). He considered the counting efficiency (using a Geiger counter in most cases) but not the time required for radiochemical separations. We have modified Schindewolf's values in order to make a comparison of the sensitivity of radioactivation analysis with that of conventional methods. His 10-hour irradiation values were changed to include a 30-minute decay period (for chemical separation) after the end of neutron irradiation, and then were multiplied by a gross normalizing factor of 2 to cover chemical yield. While 30 minutes may not be sufficient for

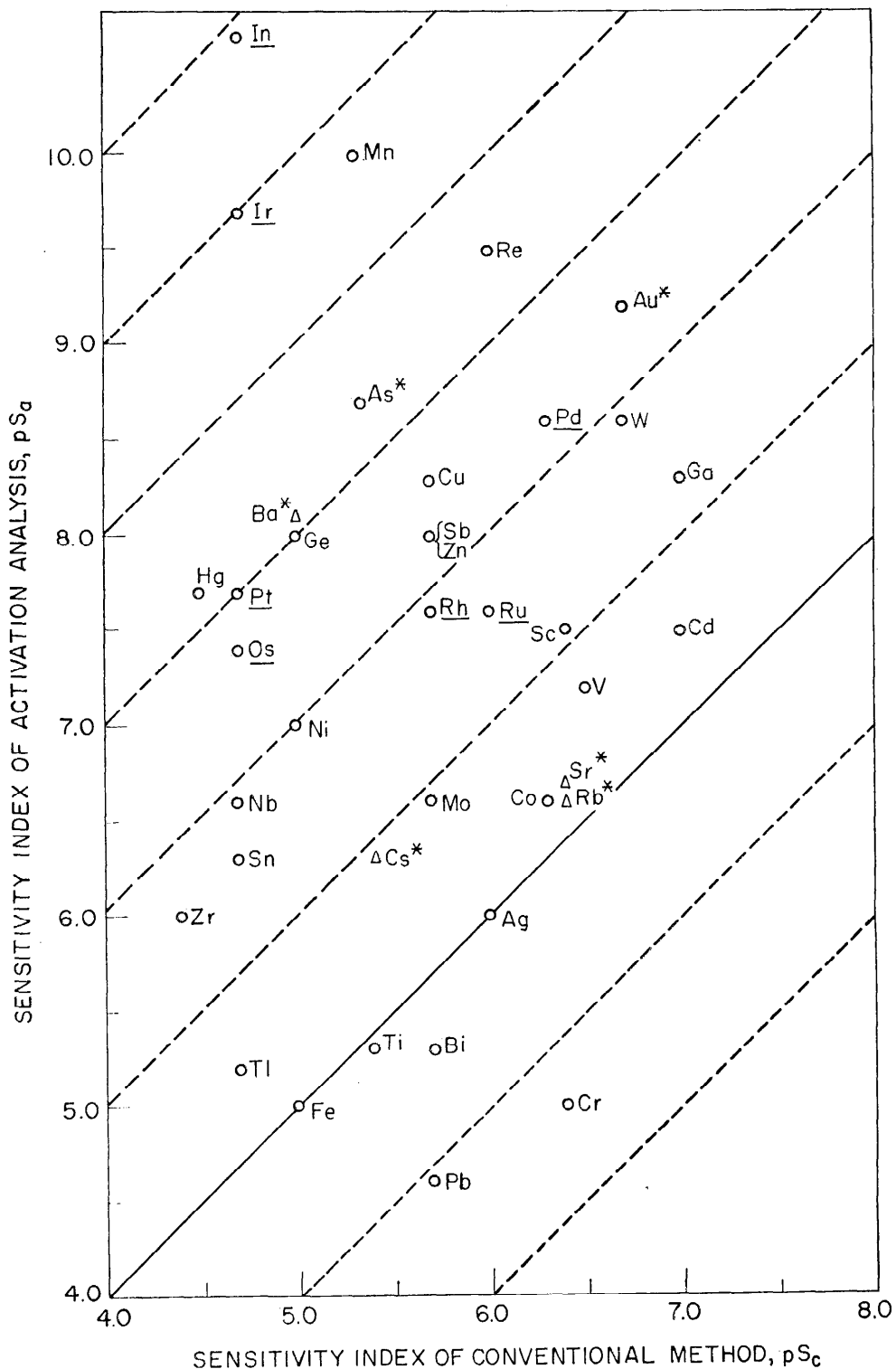


FIG. 1. Comparison of sensitivity of activation analysis with that of conventional methods. ○ spectrophotometric; △ flame photometric; \* activation analysis has already been used.

the radiochemical separation in some cases, it is reasonable time when new techniques for separation are taken into consideration. In addition, the measurement of radioactivity of some short-lived isotopes might be carried out by  $\gamma$ -spectrometry with little or no chemical separation. On the whole, the error of the sensitivities may be estimated to be about  $\pm 50\%$  or less.

For conventional methods, sensitivities quoted are mainly those of spectrophotometry (Sandell 1950), although the values of flame photometry (McInke 1955) are given for alkali metals and alkaline earths. Although various advantages may be offered by other methods, they were not included here. These sensitivity values for conventional methods were also multiplied by a factor of 2 to make them more comparable to the activation values. The maximum error of determination is estimated to be  $\pm 50\%$  or less at this level of concentration. The final volume of the solution for measurement was considered to be at least 5 ml for spectrophotometry and 2 ml for flame photometry.

In Tables 2 and 3 the sensitivities of both the activation and the conventional methods are compared. Table 2 includes all the elements of Table 1, except for the lanthanide elements and the strongly radioactive elements. Elements, other than rare gases, which had been reported neither in marine organisms nor in sea water are listed in Table 3. In these tables the unit of sensitivity is not a concentration, but an absolute weight in grams of the element in question. A "sensitivity index" was added in order to facilitate comparison of sensitivities and was defined as the negative logarithm of the sensitivity:

$$pS(\text{Sensitivity index}) = -\log S,$$

where  $S$  designates the sensitivity in grams.

In Figure 1 the sensitivity indices for activation analysis,  $pS_a$ , were plotted versus those for the conventional methods,  $pS_c$ . The solid straight line in the figure indicates the line of equal sensitivity of both methods. Therefore, the domain above the line indicates a superiority of activation analysis over the conventional methods, and *vice*

*versa*. Broken lines in the figure show 10-fold, 100-fold, etc., differences.

In some cases the sensitivity of the conventional methods might be increased by as much as a factor of 10 by using special techniques. In addition the sensitivity of the activation methods might be too high for elements giving short-lived activation products, since a detailed consideration of the radiochemical purification has not been made. Yet, the advantage offered by the application of activation methods to the analysis of a number of elements is evident. The possibility for discovery of elements of the ruthenium- or platinum-groups as well as indium in marine samples appears to be good.

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