Trace-Element Sensitivity: Comparison of Activation Analysis with Other Methods

W. Wayne Meinke

Department of Chemistry, University of Michigan, Ann Arbor

ACTIVATION analysis is a method for determining the constituents of a sample by utilizing certain nuclear properties of the isotopes of the elements in the sample. Nuclear particles are used to produce radioactive isotopes by activation of the nuclei of the sample elements. These radioisotopes can be detected and measured by their nuclear radiations. Thus with an exact knowledge of nuclear characteristics, a determination of the amount of element present can be made. This method is applicable to determination of trace elements in many types of materials used by the biologist, chemist, metallurgist, physicist, and others. Solid, as well as liquid, samples can be used for the analysis; a few milligrams or less of material is sufficient for precise work. When chemical separations are required in activation analysis to remove interfering ions, no errors are introduced by trace contaminants in the reagents.

Analysis by radioactivation was first suggested by Hevesy and Levi (*1*) in 1936 when they used neutrons from a 300-mc radium-emanation beryllium source to activate certain rare-earth elements. It was not until the advent of the nuclear reactor, however, that sources of sufficiently high neutron flux became available to give high sensitivity to this method.

In the past decade activation analysis has been viewed by many as representing the ultimate in sensitivity. The completion of new reactors with increasingly high fluxes brought a steady improvement in this sensitivity. Most analysts, however, had to forego the reportedly high sensitivities and had to use the more conventional methods of analysis because there were few reactor facilities available and access to them was limited.

In 1952 Oak Ridge National Laboratory made available to the public an activation analysis service (*2, 3*) that has since enjoyed a favorable response. At the present time several non-AEC laboratories are building research-type reactors (*4*) and the prospects for many more reactor facilities being built in the near future are good.

This increase in access and availability of sources of high neutron flux will proportionately increase the ease of obtaining analysis by activation. Not only will it be possible to send samples out to any of several laboratories for this type of analysis, but in areas near a reactor an investigator should be able to make his own analysis at the reactor facility.

Thus some critical evaluation of activation analysis as a method for determining trace quantities of elements is necessary to ascertain its advantages and limitations relative to other existing methods of trace analysis. Limits of sensitivity for various methods can be found in the literature. Although these limits vary with investigators, types of equipment, experimental procedure, and so forth, rough comparisons of these limits for each element can provide invaluable insight into the value of activation analysis relative to other methods of trace analysis.

Activation analysis. A number of general papers (*5–15*) on activation analysis should be consulted for background information on the method. The general equation governing analysis by activation is

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

where Act. is the activity (disintegrations/min); at.wt. is the atomic weight of isotope activated; f is the flux of neutrons (neutrons/cm^2 sec); (σ_{at}) is the atomic cross section of element—that is the isotopic cross section × percentage abundance of isotope (the cross section is a measure of the probability of activation for a particular isotope; a compilation of isotopic cross sections can be found in the literature); and $\left(1 - e^{\frac{-0.693t}{t_{1/2}}}\right)$ is the saturation factor which depends upon the ratio between length of bombardment and the length of half-life of the isotope formed; t is the time of bombardment; and $t_{1/2}$ is the half-life of isotope produced.

From this equation it can be seen that the activity for a given number of grams of material is directly proportional to the neutron flux. Furthermore, the number of grams of a material that gives a specified activity is inversely proportional to the flux. Thus the higher the neutron flux, the higher the sensitivity for detection of a given isotope.

Table 1 is a list of the average thermal neutron flux available from different sources of neutrons. A corollary to the fact that higher neutron fluxes give higher

Table 1. Neutron sources and usable flux (in n/cm^2 sec).

Ra-Be, 25 mg		$10^2 - 10^3$
Sb$_7$Be, 1 c		$10^3 - 10^4$
Van de Graaf		$10^7 - 5 \times 10^9$
Cyclotron		$10^8 - 10^9$
Reactor		
Oak Ridge	X-10	5×10^{11}
Oak Ridge	LITR	1×10^{13}
Brookhaven	BNL	2×10^{12}
Chalk River	NRX	2×10^{13}
Idaho	MTR	2×10^{14}

sensitivities is the fact that lower level neutron sources can be used whenever lower sensitivities can be tolerated for an analysis. Hence even the portable low-level radium-beryllium and antimony-beryllium sources can be used for analysis on occasion (*10, 16*).

Order of magnitude sensitivities of various elements for activation analysis in the 5×10^{11} neutrons/cm^2 sec flux of the Oak Ridge X-10 reactor have been published (*2*). The sensitivities are shown in Figs. 1–4 (*17*). One additional chart could be made showing only europium and dysprosium with a sensitivity of 10^{-5} μg or less for the X-10 reactor. Values for higher flux reactors are also listed on the charts.

Comparisons. Table 2 is a comparison of the sensitivities for the elements reported for activation analysis by Leddicotte and Reynolds (*9*) with those for five other typical trace analysis methods for solutions and soluble salts. These methods do not necessarily represent the five best methods for trace analysis but were chosen as typical methods in general use.

It was necessary to make a number of assumptions in order to make the comparison. Lists of sensitivity limits as published by an authority in the field were taken without any further individual evaluation. Higher sensitivities for one element or group of elements may now be possible because of recent perfection of new procedures. In addition sensitivities for an entire method might be increased by suitable improvements in technique. Neither of these possibilities has been taken into consideration in making these comparisons. Gross normalizing factors were introduced for each method to adjust the values to the same units as the activation analysis values.

The problem of interfering ions and the necessity, in some cases, for chemical separations before the indicated sensitivity can be obtained are completely neglected even though they play a very important practical role in the problem. The speed with which the analyses are made is not considered. Finally the problem of multiple-element analysis in a single sample is not considered.

Regardless of these limitations, the comparison is worth while in that it readily points out the few elements for which activation analysis is particularly well suited and also the few for which it is not. It also shows elements for which activation gives only relatively fair sensitivity but for which it is very useful because other methods are at present much less sensitive.

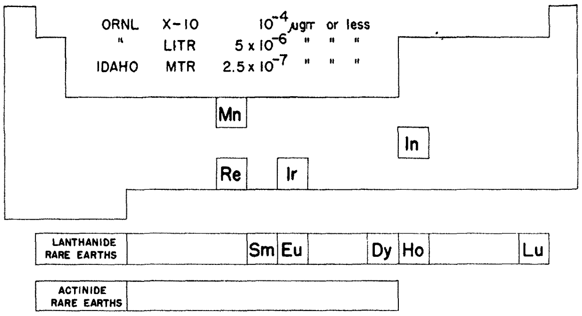

Fig. 1. Elements with thermal neutron activation sensitivity of 10^{-4} μg or less in the Oak Ridge X-10 reactor.

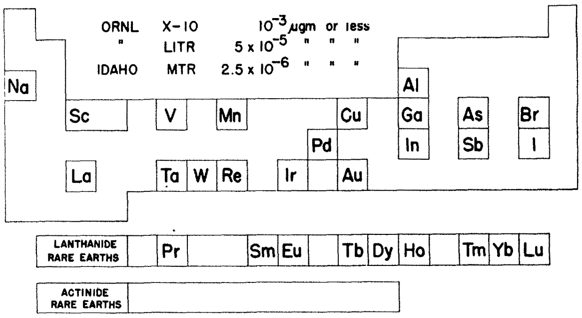

Fig. 2. Elements with thermal neutron activation sensitivity of 10^{-3} μg or less in the Oak Ridge X-10 reactor.

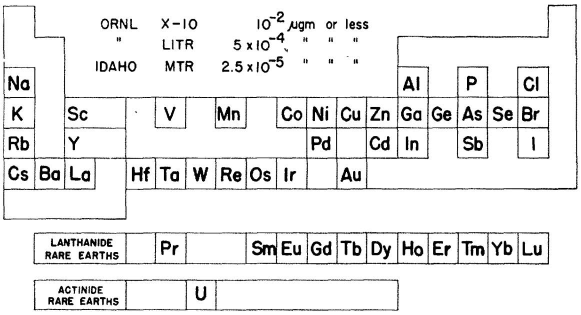

Fig. 3. Elements with thermal neutron activation sensitivity of 10^{-2} μg or less in the Oak Ridge X-10 reactor.

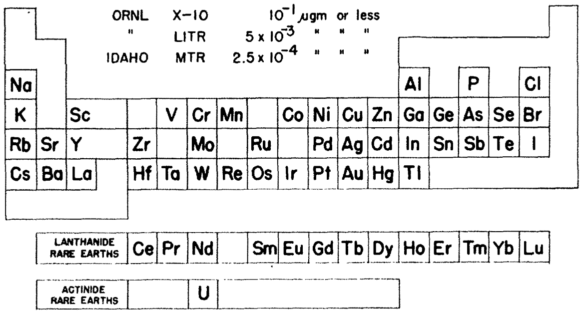

Fig. 4. Elements with thermal neutron activation sensitivity of 10^{-1} μg or less in the Oak Ridge X-10 reactor.

Table 2. Sensitivity comparisons (μg/ml).

		Methods						
Z	Element	Oak Ridge X-10 reactor	Oak Ridge LITR reactor	Copper spark	Graphite direct-current arc	Flame spectro-photometer	Sensitive color reaction	Ampero-metric titration
1	H							
2	He							
3	Li			0.002		0.02		
4	Be			.002		250.	0.04	
5	B			.1		10.		
6	C							
7	N							
8	O							
9	F			.1				0.25
10	Ne							
11	Na	0.007	0.00035	.1	20.	0.002		
12	Mg	.6	.03	.01	0.1	1.	.06	
13	Al	.001	.00005	.1	.2	20.	.002	300.
14	Si	1.	.05	.1	2.		.1	
15	P	0.02	.001	20.	50.		.01	15.
16	S	4.	.2					5.
17	Cl	0.03	.0015				.04	10.
18	A							
19	K	.08	.004	0.1		0.01		100.
20	Ca	3.8	.19	.1		.03		100.
21	Sc	0.002	.0001	.005				
22	Ti			.1		2.	.03	∼10.
23	V	.001	.00005	.05		2.	.2	3.
24	Cr	.2	.01	.05	2.	1.	.02	1.
25	Mn	.0006	.00003	.02	0.2	0.1	.001	0.0003
26	Fe	9.	.45	.5	.2	2.	.05	2.
27	Co	0.02	.001	.5		10.	.025	100.
28	Ni	.03	.0015	.1	4.	10.	.04	0.5
29	Cu	.007	.00035		0.2	0.1	.03	10.
30	Zn	.04	.002	2.	20.	2000.	.016	10.
31	Ga	.007	.00035	1.		1.		
32	Ge	.04	.002				.08	
33	As	.002	.0001	5.	10.		.1	0.4
34	Se	.05	.0025					
35	Br	.003	.00015					200.
36	Kr							
37	Rb	.03	.0015	0.2		0.1		
38	Sr	.6	.03	.5		.1		
39	Y	.01	.0005	.01		50.		
40	Zr	.3	.015	.1			.13	
41	Nb	10.	.5	.2		20.	50.	
42	Mo	0.1	.005	.05		30.	0.1	5.
43	Tc							
44	Ru	.1	.005			10.	.2	
45	Rh					1.	.2	
46	Pd	.005	.00025	.5		1.	.1	
47	Ag	.11	.0055		0.1	0.5	.1	1.
48	Cd	.05	.0025	2.	4.	20.	.01	5.
49	In	.0001	.000005	1.		1.	.2	100.
50	Sn	.2	.01		0.2	10.		2.
51	Sb	.004	.0002	5.	4.		.03	10.
52	Te	.1	.005	0.5		100.	.5	
53	I	.002	.0001					1.
54	Xe							
55	Cs	.03	.0015	.5		1.		
56	Ba	.05	.0025	.1		3.		25.
57	La	.002	.0001	.05		5.		
58	Ce	.1	.005	.5		20.	.25	∼500.
59	Pr	.002	.0001	.2		100.		

Z	Element	Methods						
		Oak Ridge X-10 reactor	Oak Ridge LITR reactor	Copper spark	Graphite direct-current arc	Flame spectrophotometer	Sensitive color reaction	Amperometric titration
60	Nd	.1	.005	.2		50.		
61	Pm							
62	Sm	.0006	.00003	.2		100.		
63	Eu	.00003	.0000015	.02				
64	Gd	.02	.001	.1		10.		
65	Tb	.004	.0002					
66	Dy	.00003	.0000015	.5		10.		
67	Ho	.0004	.00002	.2				
68	Er	.02	.001	.5				
69	Tm	.002	.0001	.05				
70	Yb	.002	.0001	.1				
71	Lu	.0003	.000015	2.				
72	Hf	.02	.001	0.5				
73	Ta	.007	.00035	1.				
74	W	.003	.00015	0.5			0.4	
75	Re	.0006	.00003	2.			.05	
76	Os	.02	.001				1.	
77	Ir	.0003	.000015	5.			2.	
78	Pt	.1	.005	0.02			0.2	
79	Au	.003	.00015	.2		200.	.1	
80	Hg	.13	.0065	5.	2.	100.	.08	
81	Tl	.6	.03		0.2	1.		
82	Pb	2.	.1	0.05	.2	20.	.03	3.
83	Bi	~ 0.4	~ .02	.2	.2	300.	1.	300.
84	Po							
85	At							
86	Em							
87	Fr							
88	Ra			.1				
89	Ac							
90	Th			.2				
91	Pa			2.				
92	U	.01	.0005	1.		10.	0.7	

In Table 2, sensitivities that can be obtained by activation analysis with two different nuclear reactors are compared with sensitivities for the other methods. Sensitivities for each element and method are those reported in the compilations of data listed here. Certain gross normalizing factors, however, were used for each method to adjust the values to the common sensitivity basis of "micrograms per milliliter" and an error of about 10 percent. It was assumed that as much as 25 or 50 ml of the unknown solution was available.

The values listed in the table represent an *order of magnitude only,* since peculiarities of experimental procedure, investigators, and so forth, introduce considerable variation. For activation analysis they represent conservative values, although values for other methods may be somewhat optimistic. Several of the methods are capable of an increase in sensitivity of a factor of 10 or more by a change of equipment or the use of larger samples, and so forth, if they were to be pushed to the limit.

The table, although not complete, is presented as a basis for general comparisons of the methods or as a type of work sheet. Pertinent information on each method follows.

Oak Ridge X-10 reactor. Values are listed by Leddicotte and Reynolds (*9*) for activation analysis in the Oak Ridge X-10 reactor at a flux of 5×10^{11} neutrons/cm^2 sec to give 40 disintegrations/sec. Samples are activated to saturation or 30 days, whichever is shorter. It is assumed that a 1-ml sample is evaporated per analysis. The sensitivity of the method could be substantially increased by increasing the volume of sample used. The primary limitation is the effect of self-absorption of the bulky sample upon the radiations emitted by the radioisotope. If it were desired to increase the sensitivity further, samples with activity less than 40 disintegrations/sec might be accepted. With special techniques an activated isotope having about one-tenth of this activity could be determined.

Oak Ridge LITR reactor. Values are given for activation analysis in the Oak Ridge LITR reactor (or proposed university research reactors at full power) at a flux of 10^{13} neutrons/cm^2 sec. All other conditions and comments are identical to those given for the X-10 reactor.

Copper spark. The original sensitivity values from which these were derived are listed by Nachtrieb (*18*) for spectrographic analysis using the copper-spark method. It is assumed that for best results only 1/20 ml of sample can be evaporated on the electrode. If more sample could be evaporated without interfering seriously with the analysis, the sensitivity relative to activation would increase. Nachtrieb gives his data in millimicrograms using a 50-lambda sample and estimating an error of ±3 to 8 percent. His values were divided by 1000 to convert to micrograms, multiplied by 20 to adjust to the basis of a 1-ml sample, and divided by 2 to allow for an error of ±10 percent. The net result was to divide the literature values by 100 for the comparison.

Graphite direct-current arc. The original values are also listed by Nachtrieb (*18*) for spectrographic analysis using graphite direct-current arc methods. It is assumed that 1/20 ml of sample was evaporated on the electrode. All comments on normalization given for the copper-spark method apply to this method. The literature values were divided by 100 to obtain the comparison value.

Flame spectrophotometer. The original sensitivity values for analysis using the flame spectrophotometer with an oxyhydrogen flame are given in Beckman Reprint R-56 (*19*). Values were given directly in micrograms per milliliter. The errors given for the reported sensitivities were ±100 percent. The values were therefore multiplied by a normalizing factor of 10 to convert them to the same ±10 percent error as the other methods.

Sensitive color reaction. The original sensitivity values for spectrophotometric analysis using sensitive color reactions were taken from Sandell (*20*). The values are given in micrograms per square centimeter. It was assumed that a standard 1-cm cell was used in the spectrophotometer, although the 10-cm cells available could increase the sensitivity by a factor of 10. As in the case of flame photometry, the original values were given with a ±100-percent error and were multiplied by a normalizing factor of 10 to convert to the prescribed basis.

Amperometric titration. The original values for amperometric titration are listed in a compilation made by Sargent and Co. (*21*). These values were not all converted to the same units in the compilation; some were given as micrograms, others as molarity, and so forth, with different limits of error. For this comparison, the sensitivity values were converted as nearly as possible to the common basis of the other methods considered. The normalized values, however, are much less certain than values presented for the other methods. Recent work on coulometric analysis may have superseded some of the lower sensitivity values for a number of the elements.

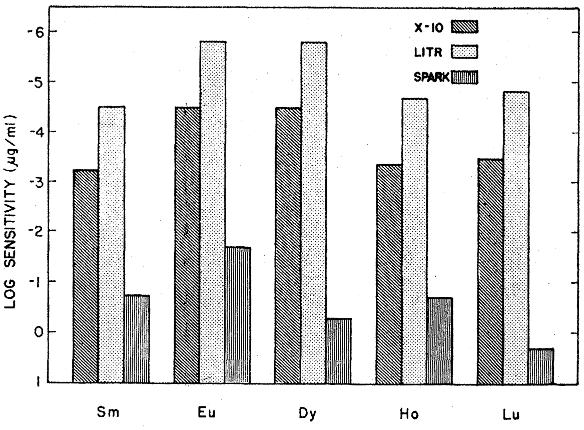

Fig. 5. Comparison graphs of some rare earth elements having high sensitivity for activation analysis.

Comparison graphs. Comparisons of these methods can be seen much more readily when they are presented in graphic form. Therefore methods for certain elements of importance have been compared graphically.

Certain of the rare-earth elements show the highest sensitivity of any elements for activation analysis. These are shown in Fig. 5 compared with the values for spark spectroscopy. For europium and dysprosium truly fantastic sensitivities can be obtained. For each of the elements shown in this figure, analysis by activation so far overshadows other methods that it is possible to obtain sensitive analysis with neutron fluxes much lower than those of a reactor.

Manganese, indium, rhenium, and iridium are four other elements that show high sensitivity on the chart

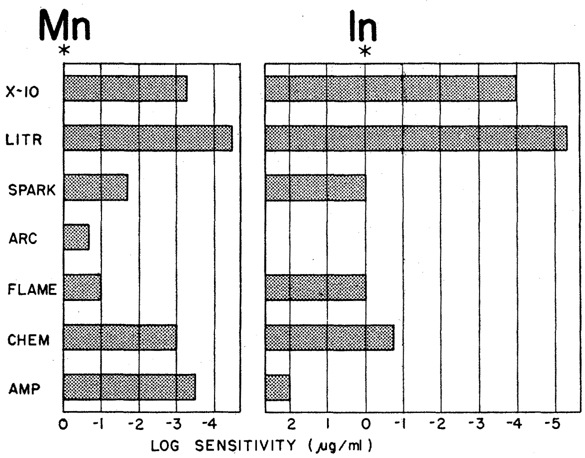

Fig. 6. Comparison graphs for manganese and indium.

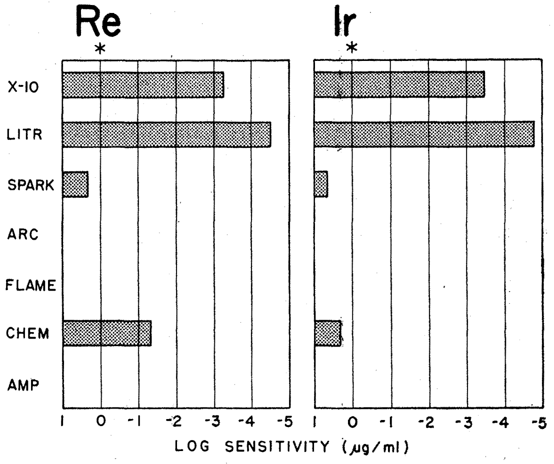

Fig. 7. Comparison graphs for rhenium and iridium.

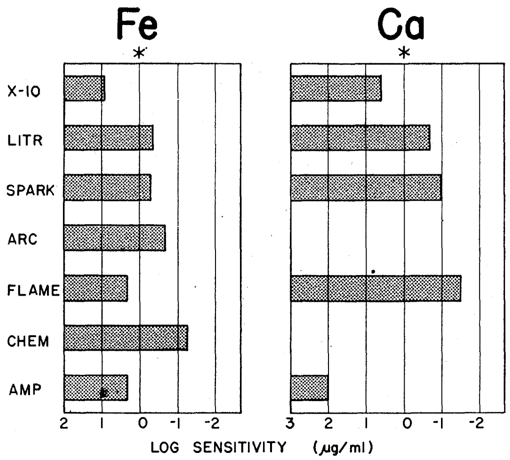

Fig. 8. Comparison graphs for iron and calcium.

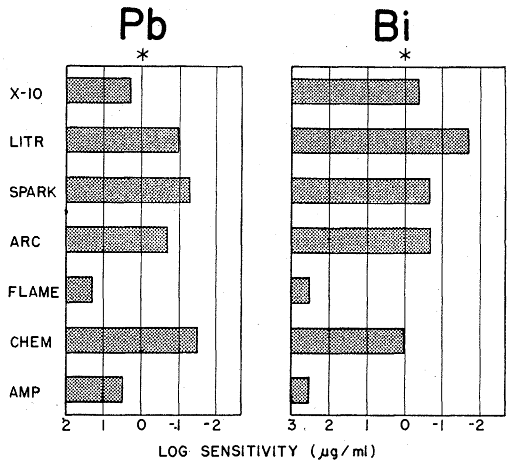

Fig. 9. Comparison graphs for lead and bismuth.

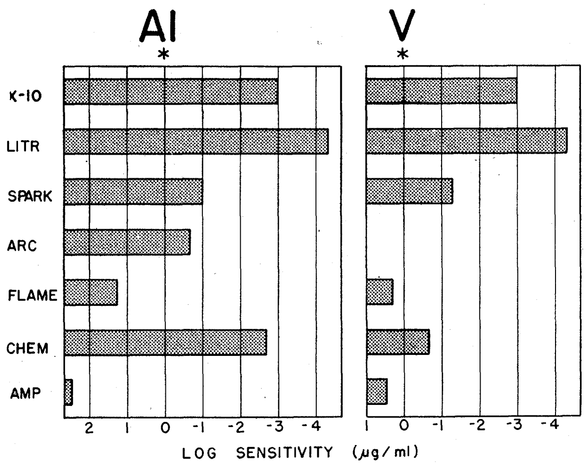

Fig. 10. Comparison graphs for aluminum and vanadium.

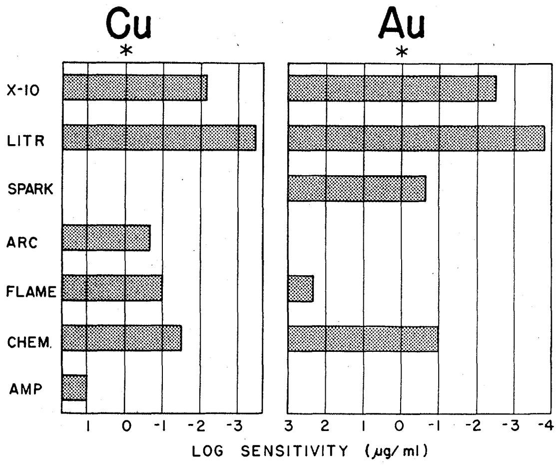

Fig. 11. Comparison graphs for copper and gold.

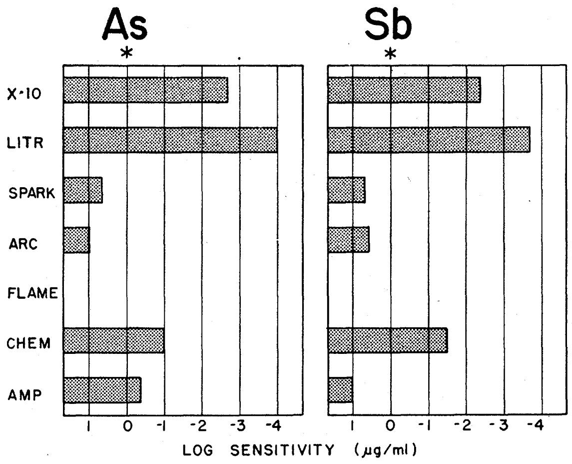

Fig. 12. Comparison graphs for arsenic and antimony.

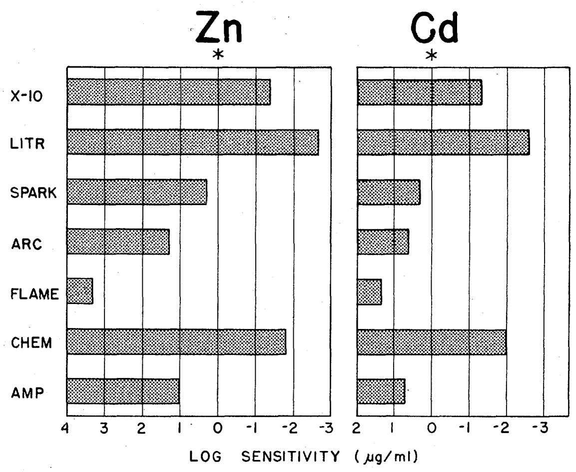

Fig. 13. Comparison graphs for zinc and cadmium.

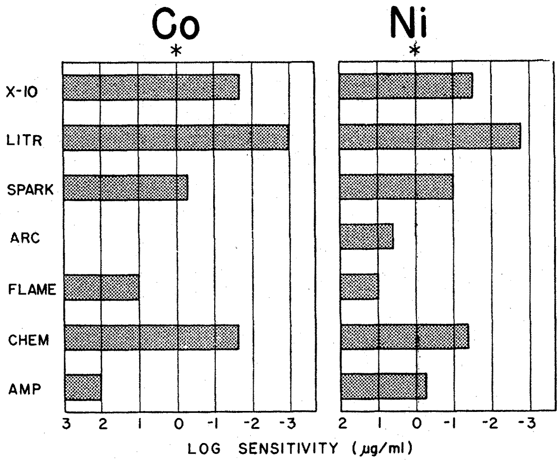

Fig. 14. Comparison graphs for cobalt and nickel.

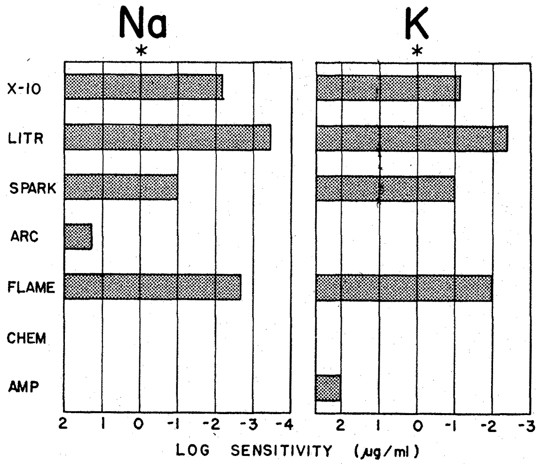

Fig. 15. Comparison graphs for sodium and potassium.

of Fig. 1. The sensitivities for these elements are plotted in Figs 6 and 7. The stars on the graph under the symbol of the element indicate the zero point on the log sensitivity scale. Although activation analysis is very sensitive for manganese, the coulometric method of Furman and the spectrophotometric method using 4,4′-tetramethyldiaminotriphenylmethane give almost equivalent sensitivities. For indium, on the other hand, the other methods are not as highly developed, and activation would prove very useful. Activation would also prove invaluable for both rhenium and iridium, since other methods available at present prove unsatisfactory for highest sensitivity.

Figures 8 and 9 show comparison graphs for iron, calcium, lead, and bismuth, all of which show poor sensitivity for activation analysis. For analysis of these elements, it would be inadvisable to use activation analysis unless some special condition required it.

Table 3. Reagents for high sensitivity color reactions (*19*).

Element	Reagent
Mn	4,4′-Tetramethyldiaminotriphenylmethane
In	8-Hydroxyquinoline
Re	Thiocyanate-stannous chloride (ether solution)
Ir	$IrCl_6^{=}$
Fe	*o*-Phenanthroline
Ca	
Pb	Dithizone (CCl_4)
Bi	Phenyldithiobiazolonethiol
V	Benzoylphenylhydroxylamine
Cu	Dithizone (CCl_4)
Au	*o*-Tolidine
As	Molybdate-hydrazine sulfate
Sb	Rhodamine B
Zn	Dithizone (CCl_4)
Cd	Dithizone (CCl_4)
Co	Nitroso R-salt
Ni	Bromine-dimethylglyoxime
Na	
K	
Al	Oxine

Figures 10, 11, and 12 show graphs for aluminum, vanadium, copper, gold, arsenic, and antimony, all of which show good sensitivity for activation analysis. Activation does not present enough advantage over conventional methods to warrant its use for copper and aluminum, but for the others it may provide some advantage.

Figures 13, 14, and 15 show graphs of several other elements that are either neighbors in the periodic table or are in the same family. For each the activation sensitivity is only fair but in some cases the method would be advantageous.

Table 3 lists the chemicals that are reported to give the sensitivities indicated for the sensitive-color-reaction method on the graphs of Figs. 6–15.

Summary. Rough comparisons of the sensitivity of activation analysis with other standard methods give the investigator a feel for the elements for which activation can be used as a powerful tool. Although improvements in technique for an entire method or for an individual element will invalidate the figures given in Table 2, the over-all picture will be changed only slightly. Furthermore, other considerations such as speed of analysis, interferences of other elements, and availability of analyzing instruments and facilities may indicate the use of one method in preference to another. The increasing availability of nuclear reactor facilities, however, means that analysis by activation is an important new tool for general use in trace analysis (*21*).

References and Notes

1. G. V. Hevesy and H. Levi, *Kgl. Danske Videnskab. Selskab. Matfys. Medd.* **14**, 5 (1936) ; **15**, 11 (1938).
2. ———, *Isotopics* **2**, No. 2, 4 (1952). Isotopics is a publication of the Isotopes Division, U.S. AEC, Oak Ridge, Tenn.
3. W. J. Murphy, *Anal Chem.* **24**, 1235 (1952).

4. ———, *Nucleonics* **12**, No. 4, 7 (1954).
5. G. E. Boyd, "Method of activation analysis," *Anal. Chem.* **21**, 335 (1949); AECD-2507 (Mar. 1949).
6. W. A. Brooksbank, G. W. Leddicotte, and H. A. Mahlman, "Analysis for trace impurities by neutron activation," *J. Phys. Chem.* **57**, 815 (1953).
7. E. A. Burrill and A. J. Gale, "Activation analysis with Van de Graaf neutron sources," pamphlet, High Voltage Engineering Corp., Cambridge, Mass., May 1954.
8. G. W. Leddicotte and S. A. Reynolds, "Activation analysis with the Oak Ridge reactor," *Nucleonics* **8**, No. 3, 62 (1951).
9. G. W. Leddicotte and S. A. Reynolds, "Neutron activation analysis; a useful analytical method for determination of trace elements," U.S. Atomic Energy Comm., AECD-3489 (Jan. 1953).
10. W. W. Meinke and R. E. Anderson, "Activation analysis using low level neutron sources," *Anal. Chem.* **25**, 778 (1953).
11. C. O. Muehlahuse and G. E. Thomas, "Use of the pile for chemical analysis," *Nucleonics* **7**, No. 1, 9 (1950).
12. F. E. Senftle and W. Z. Leavitt, "Activities produced by thermal neutrons," *Nucleonics* **6**, No. 5, 54 (1950).
13. A. A. Smales, "Radioactivation analysis," *Ann. Repts. Chem. Soc. for 1949* **46**, 285 (1950).
14. A. A. Smales, "The scope of radioactivation analysis," *Atomics* **4**, No. 3, 55 (1953).
15. T. I. Taylor and W. W. Havens, Jr., "Neutrons spectroscopy for chemical analysis—III," *Nucleonics* **6**, No. 4, 54 (1950).
16. W. W. Meinke and R. E. Anderson, *Anal. Chem.* **26**, 907 (1954).
17. Thanks are due to G. W. Leddicotte and S. A. Reynolds for permission to extend their sensitivity chart (*9*) in Figs. 1–4. Two changes could be made in the charts to bring them up to date. The detection limit for nickel should be 1 μg, and thorium should be added to the figures with a limit of 10^{-3} μg.
18. N. H. Nachtrieb, *Principles and Practice of Spectrochemical Analysis* (McGraw-Hill, New York, 1950), p. 272.
19. Beckman Reprint R-56. (Industrial Laboratories, August 1952.) Beckman Instruments, Inc., South Pasadena, California.
20. E. B. Sandell, Colorimetric Determination of Traces of Metals, *3*, Second Edition (1950), p. 648, Interscience Publishers, Inc., New York.
21. "Technique of amperometric titration," Sargent Scientific Methods, Fall 1953, p. 10, E. H. Sargent and Co., Chicago, Ill.
22. This work and similar studies on activation analysis have been supported in part by the University of Michigan Memorial Phoenix Project. The assistance of Kenneth K. Kendall, Jr., of Beckman Instruments Inc., A. A. Shurkus of Applied Research Laboratories, and C. E. Shuter of Jarrell-Ash Co., in locating authoritative summaries of sensitivities for standard methods of analysis is gratefully acknowledged. The material given in this paper was presented before the Gordon Research Conference in Analytical Chemistry at New Hampton, N. H., in Aug. 1954.

The Scientist as a Citizen

J. R. Schenken

University of Nebraska, College of Medicine, Omaha

SCIENTIFIC meetings in general, and particularly medical meetings, are rightfully dominated by the philosophy of René Descartes, who provided a guiding spirit in the 17th century when he wrote:

> I am sure that there is no one, even among those who make its [medicine's] study a profession who does not confess that all that men know is almost nothing in comparison with what remains to be known. I judge there was no better provision against a short life or lack of experience than faithfully to communicate to the public the little which I should myself have discovered, and to beg all well inclined persons to proceed further and then to communicate to the public all the things which they might discover in order that the last should commence where the preceding had left off, and thus by joining together the lives and labors of many, we should collectively proceed much further than anyone in particular could succeed in doing.

But the present complicated problems of our world—a world in which conflicting ideologies threaten the very existence of what we call Western Civilization, and a world in which scientific specialists are fortunate to be able to meet in an atmosphere free from government restrictions, military censorship, or the security surveillance of secret police—call for more than a dedication of our intellects and our labors to mankind.

In order that we may continue as a free society, every person must know and follow the basic principles of responsible individualism that have made our present achievements possible. The present technologic era began sometime in the 18th century, when wealth and science were united amid the clamor of men and women who since the Renaissance had regained their will to be free from political and spiritual enslavement.

A new man was created and mass production became the order of the day. The artisan became a specialist in labor and virtually became part of a machine. In the process of this metamorphosis he lost much of his imagination and creativeness. Such a man is restless because he has no impelling objectives in life. He fears the future because his talents are limited; he looks to society for his rights, and in so doing, he is in danger of losing his obligations. He avoids "travel along the road, and is attracted to the Inn," as Cervantes puts it, where he can sit with self-satisfaction because he has no goal—no place to go.

Ortega was proud but somewhat alarmed at his Spanish countryman who, instead of merely pointing the way, readily escorted the inquiring foreign visitor to the point of inquiry, and thereby left a favorable impression of extreme courtesy. Ortega wonders if this act was a sign of national pride, or was it in reality a sign that his countryman had no mission in