Talanta, 1972, Vol. 19, pp. 163 to 172. Pergamon Press. Printed in Northern Ireland

PRECONCENTRATION TECHNIQUES FOR TRACE ANALYSIS *VIA* NEUTRON ACTIVATION

J. MARK ROTTSCHAFER*
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

and

RONALD J. BOCZKOWSKI and HARRY B. MARK, JR.
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(*Received* 5 *July* 1971. *Accepted* 1 *October* 1971)

Summary—A review is given of the methods that have been proposed for enrichment of trace elements in samples that are to be analysed by neutron-activation methods. The emphasis is on classification of methods, with full illustrations by means of practical examples.

THE RECENT CONCERN over metal pollutants in the environment has resulted in increased efforts to develop satisfactory analytical procedures for determining trace metals in natural systems. The fact that many metals are found at low concentration levels in biological or other natural systems has imposed serious limitations on the analytical techniques that can be applied to direct determination of these trace metals.

Neutron-activation analysis (NAA), because of its inherent sensitivity, has become a prime technique for trace analysis.[1] The sensitivity of this technique for a number of elements is 1 part per milliard (ppM)[2,3] and under ideal conditions can be as low as one part in 10^{12}.[4] Despite this great sensitivity, the necessary procedures for using NAA for trace metal analysis will, in many cases, limit the actual concentration levels that can accurately be determined.

A good example of this is the use of NAA to determine metal ion concentrations in blood or sea-water samples where the metal species may be present in concentrations of 10^{-6}–$10^{-12}M$.[5,6] Since the metal or metals of interest are at such low concentrations, it is necessary to irradiate a large volume of sample in order to achieve a sufficient count rate. The bulk matrix, however, may absorb neutrons and thereby shield the trace elements of interest from activation.[7] Furthermore, the matrix itself may become highly radioactive and obscure the activity of the trace metals present. This latter fact is especially true for sea-water and biological samples in which large amounts of ^{24}Na are produced on irradiation. These various factors combine to reduce the sensitivity of NAA for trace metals in such systems.

One solution to such problems is to separate and isolate trace metals from the bulk matrix after irradiation. "Hot" chemical separation is a technique commonly employed to allow the determination of a metal when other interfering radionuclides may be present after irradiation.[6] While such a technique might be useful, there are significant difficulties associated with its use. Special facilities and equipment are required to handle radioactive samples for separation procedures. In the case of short-lived nuclides, the time required for chemical separation may be of such a length as to completely preclude the use of this technique.

An alternative procedure which has been effectively employed is to separate and

* Present address: BASF-Wyandotte Chemicals Corp., Wyandotte, Michigan 48192.

concentrate the desired species from the bulk matrix before irradiation. The problems of handling "hot" solutions are eliminated and the concentrated sample can more conveniently be determined by NAA. However, great care is necessary to avoid introducing impurities (at the level contained by the sample or even more) from reagents, etc, during the preconcentration procedure. Such preconcentration methods have been both widely and successfully used and are reviewed here.

Taylor[8] has discussed in detail several methods of preconcentration used in conjunction with NAA to analyse for trace elements in blood, cerebrospinal fluid and urine. Among the methods discussed were column chromatography, electrophoresis and ultracentrifugation. Joyner *et al.*[9] published a review and an evaluation of preconcentration methods used with a number of analytical techniques for the determination of trace metals in sea-water. These previous reviews have presented only a few examples of the application of preconcentration techniques to NAA. This paper is intended as a general review of the subject without including references cited in the reviews mentioned above.

CHROMATOGRAPHIC METHODS

Chromatographic methods are ideally suited for preconcentration and offer the added advantage of being able to isolate the concentrated species as pure components. The following describes the various chromatographic techniques that have been applied to the preconcentrating of species for determination by NAA.

Ion-exchange chromatography

Ion-exchange chromatography has been used extensively both alone and in conjunction with other techniques to concentrate and separate elements for NAA. In the biomedical field it has been used to determine protein-bound iodine in human blood and plasma. The usual technique involves passing the sample through an anion-exchanging resin[10] to remove inorganic iodide or through a mixed-bed resin[11] to remove iodide and non-protein-bound electrolytes. The effluent containing the protein-bound iodide is then irradiated and analysed. Hamada and co-workers[12] varied this procedure slightly by oxidizing the effluent with chromic acid and distilling the iodine produced into a potassium hydroxide solution. This solution was evaporated to dryness and the residue irradiated.

Total organic iodine,[13] free thyroxine[14] and total thyroxine[15] in human serum have been determined after separation by ion-exchange. Zaichik *et al.*[16] have designed a scheme for the determination of free iodide, and hormonal and non-hormonal iodide in blood serum. Free iodide is removed from the sample with Dowex-1 and eluted (A). Organic iodide is sorbed on Dowex 50. Non-hormonal iodide can be eluted from the resin with water (B) and hormonal iodide eluted with a buffer at pH 2 (C). Samples A, B and C are then lyophilized and irradiated.

Inorganic iodide has been separated from urine on an anion-exchanging resin.[17,18] In one example, the iodide can be selectively eluted for irradiation.[17] In another, after the elution of bromide and chloride ions, the resin is dried and irradiated directly.[18] Direct irradiation of the resin has also been applied to determine inorganic fluoride in urine.[19]

In another biochemical application,[20] selenocystathionine was extracted from nuts. The extract was passed through a Dowex-1 column and the fractions irradiated for determination.

Ion-exchange has been particularly useful in preconcentrating elements from natural water systems since essentially unlimited volumes can be passed through a column to obtain the desired sensitivity. Examples are given below.

Rubidium and caesium concentrations in the North Atlantic[21] and vanadium in the Colorado River[22] and in other natural water systems[23] have been determined by concentrating the elements on cation-exchanging resin. After elution from the column the sample is evaporated and irradiated. A similar technique has been used to determine silver ion present in samples of the rain water produced by cloud seeding with silver iodide.[24] A sensitivity of 10^{-10} g is reported. ^{230}Th and ^{232}Th have also been determined in natural water systems.[25] After cation-exchange concentration and elution with EDTA, the thorium is co-precipitated with titanium hydroxide for irradiation.

An anion-exchanging resin can be used for preconcentration of elements which form anionic complexes. Rhenium (as perrhenate ion) in sea-water,[26] and molybdenum and manganese present in solution as the molybdate and permanganate ions[27] have been determined by this method after elution from the column. Chromate ion in the ppM range in water[28] and mercury present in urine[29] have also been preconcentrated on anion-exchanging resin. In both cases the resin was irradiated directly without elution.

Similarly ion-exchanging membranes have been used as a preconcentration matrix for cations in aqueous solutions.[30–32] The procedure is to stir pieces of membrane in the solution, allowing sufficient time to reach equilibrium or to obtain sufficient metal concentration in the membrane for analysis. The membranes are then dried and irradiated. Green *et al.*[33] were able to determine ppM quantities of gold by using paper loaded with 50% Ionac SRXL resin (a resin specific for gold and the platinum group metals).

Paper chromatography

The technique of paper chromatography has also been widely used as a means of preconcentration. It offers an advantage in that the paper chromatogram containing the isolated species can itself be irradiated without further preparatory steps. This method has been notably successful in determining organic and biologically-related compounds.

While first row elements, such as hydrogen, carbon, oxygen, or nitrogen are not suitable for NAA, many of the organic and biologically related compounds contain elements such as sulphur, phosphorus, chlorine, or bromine that can be activated, and therefore be determined by NAA.

By this method phospholipids have been determined in human blood serum and spermatozoa,[34] in liver bile,[35] and in liver biopsy specimens and plasma.[36] Phospholipids have also been separated on paper and determined by NAA after extraction from cerebrospinal fluid and concentration on a silic acid column.[37] Strickland and Benson[38] were able to determine phosphatides after extracting them from cell fractions, converting them into phosphate diesters and separating them on paper. Phosphoryl peptides in protein[39] and mono- and oligonucleotides in calf thymus DNA and MS2-RNA have been determined after electrophoretic paper chromatography separation.[40] The purity of phosphate nutrient solutions for botanical use have even been determined with use of a paper chromatography preconcentration step.[41]

Schmeiser and Jerchel[42,43] have determined biologically-related compounds containing sulphur, chlorine, bromine and phosphorus. Skinner *et al.*[44] have determined chlorine- and bromine-containing drugs after separation and preconcentration by paper chromatography. Iodostyrine[45] and other iodo-compounds[46] in blood serum have been separated and determined. Certain organobromine compounds have been found in deproteinized spinal fluid.[47] Bromine analogues of DDT have also been separated for analysis.[48,49] Iodine and iodine compounds,[50] including isomers of di-iodobenzoles,[51] have been separated from aqueous solutions and determined by NAA.

If the compound to be determined does not contain an element suitable for activation, derivatives can be prepared which will contain a suitable nuclide. Steim and Benson[52] prepared bromine derivatives of amino-acids, carboxylic acids, keto-acids and sugars for paper chromatographic separation and irradiation. Unsaturated fatty acids in the form of mercury complexes have also been separated and determined by these authors.[52]

Metal ions and metal-containing compounds have also been isolated for analysis by paper chromatography. Cobalt and vanadium were determined on paper chromatograms after tissue samples were ashed, dissolved and chromatographed before NAA.[34] After homogenization and deproteinization of serum, muscle and liver tissue, selenomethionine was separated from other components and determined.[53] Sodium, uranium and the lanthanide elements have been separated by ascending paper chromatography on Whatman No. 1 filter paper with mixtures of alcohol and nitric acid to develop the chromatogram.[54,55] The chromatogram strips were irradiated for analysis.

Zinc[56] and magnesium[57,58] present in aqueous solutions were determined by NAA after chromatographic preconcentration. These metal ions were extracted from aqueous solutions into chloroform by complexation with 5,7-dibromo-8-hydroxyquinoline. The metal complexes were separated from excess of chelating agent by paper chromatography. Though zinc could be determined from the activity of the ^{65}Zn produced on irradiation, magnesium, having a low abundance of the isotope that can be activated and a low thermal neutron cross-section ($^{26}Mg = 11\%$, $\sigma = 0{\cdot}03$ barn),[59] could not be determined from ^{27}Mg. This difficulty was obviated by determining the activity of ^{82}Br produced ($^{81}Br = 50\%$, $\sigma = 3{\cdot}0$ barn)[59] when the magnesium complex was irradiated and hence indirectly the amount of magnesium present.

Miscellaneous chromatographic methods

Other chromatographic methods of preconcentration have also been applied to NAA. Column chromatography has been used to separate chlorine- and bromine-containing drugs[44] and to collect phospholipids extracted from cerebrospinal fluid.[37] Thin-layer chromatography has been used to separate mercurous and mercuric ions from other cations.[60] Following this, a section of the substrate containing these mercury species was taken for NAA.

Protein-bound elements have been separated from other materials present in blood serum by gel permeation chromatography. Fritze and Robertson[61] have determined a large number of protein-bound metals by freeze-drying the protein fraction of the eluate, irradiating and then either determining the activity directly or

after a radiochemical separation. Protein-bound copper[62] and iodine[63] have also been preconcentrated for NAA by using gel permeation chromatography.

EXTRACTION METHODS

Solvent extraction has often been used as a means of preconcentration. Vanadium in blood samples[64,65] has been determined by extracting with 8-hydroquinoline, evaporating the solvent and irradiating the residue for analysis. Thenoyltrifluoroacetone has been used to extract calcium, copper, magnesium and manganese from serum[66] into a tetrahydrofuran/benzene solution. NAA of these metals was performed after re-extracting the metals into a small volume of nitric acid and irradiating. Selenium in biological materials[67] was isolated for analysis by first drying the sample and then oxidizing it with nitric acid and hydrogen peroxide and finally extracting the selenium with 8-mercaptoquinoline.

The use of solvent extraction in conjunction with other techniques for preconcentration has also been cited in the literature. As an initial step, before further fractionation, solvent extraction has been used to separate phospholipids from cerebrospinal fluid[37] and phosphatides from cell functions.[38] A determination of selenocystathionine in nuts[20] was obtained after an initial extraction followed by fractionation on an ion-exchange resin and irradiation.

Solvent extraction has proved to be useful in isolating metals from sea-water or aqueous solutions after chelation of the metal. Using sea-water samples, extractions have been made of copper, manganese and zinc with diethyldithiocarbamate into chloroform,[68,69] uranium with tri-n-octylphosphine oxide into cyclohexane[70] and vanadium with α-benzoinoxime into benzene.[71] In each case the solvent was evaporated and the residue irradiated for analysis. Zinc[56] and magnesium[57,58] were extracted from aqueous solutions into chloroform as the 5,7-dibromo-8-hydroxyquinolinates and separated from excess of chelating agent and solvent by paper chromatography before irradiation. In a similar application, a mercury dithizone complex was extracted into chloroform and the solution evaporated on plastic film which was irradiated directly.[72] This method appears to have the added advantage of preventing mercury volatilization losses since mercury tends to react with unsaturated bonds in the plastic film.[73]

Extraction methods can also be employed to remove impurities or interfering nuclides before determination. Uranium, for example, has been removed from solutions by complexing with tributyl phosphate and extracting. This allowed trace amounts of copper, cobalt and manganese in the original solution to be determined.[74]

PRECIPITATION METHODS

Both precipitation and co-precipitation have been used to remove trace elements from bulk solution. When irradiating a precipitate directly, it is necessary that neither the precipitating agent nor the co-precipitant contain nuclides with an activity which would interfere in the determination. A common procedure to circumvent this problem is the separation of the element of interest from the precipitate and its conversion into a form more suitable for analysis.

Rona *et al.*[75] coprecipitated manganese and zinc from sea-water with hydrous ferric oxide. After dissolution of the separated precipitate with hydrochloric acid, iron as the trichloride was removed from the solution by extracting with isopropyl ether. The aqueous phase was evaporated to dryness and the residue then irradiated

and analysed. A similar procedure has been employed in the determination of ruthenium in sea-water.[76] After precipitation and extraction of the iron from the dissolved precipitate as described above, the hydrochloric acid solution is evaporated. The residue is redissolved in a potassium permanganate–sulphuric acid solution and from it ruthenium oxide is distilled into hydrochloric acid for subsequent irradiation and determination. The lanthanide elements have also been co-precipitated with hydrous ferric oxide.[77–80] After dissolution of the precipitate in hydrochloric acid and extraction of the iron, uranium and thorium are removed by anion-exchange and the eluate is evaporated for irradiation.

In a few instances it has been possible to irradiate the ferric hydroxide precipitates directly in order to determine co-precipitated metals without removal of the iron. This method has been applied to determine tantalum in sea-water,[81] thorium in mineral springs and Japanese coastal waters,[82] and indium in rain water.[83]

Calcium oxalate has been employed as a co-precipitant and used to precipitate barium and strontium from urine,[84] strontium from sea-water,[85] and several rare-earth elements from hot spring water.[86] After separation and drying, the precipitate was irradiated directly.

A number of instances have been reported of precipitating metal ions with an appropriate anion of a soluble salt. Cobalt, zinc and uranium in sea-water have been precipitated in this manner with disodium phosphate.[87] The precipitate was then dissolved in acid and passed through cation- and anion-exchanging columns to separate the metals for irradiation and NAA. Thorium in urine has been determined by adding ammonia solution to an acidified urine sample and irradiating the resultant precipitate.[88] By a precipitation method, uranium in milk has been determined to one part in 10^{12}.[89] The procedure entailed drying and ashing the milk, dissolving the residue in hydrochloric acid and precipitating the uranium with sodium ferrocyanide.

An unusual determination of ^{18}O in water has been accomplished by converting the oxygen into carbon dioxide and thence into solid ammonium carbonate which is irradiated.[90] With suitable modification, this method could be applied to the determination of tagged organic or biological materials in aqueous solutions.

DRYING AND ASHING METHODS

Perhaps the simplest methods of concentration are evaporation or freeze-drying of an aqueous sample and ashing of a solid sample. Evaporation and freeze-drying have been applied to the analyses of lake water,[91,92] sea-water,[93,94] mineral spring water[95] and Rhine river water.[96] Aluminium in reactor cooling water[97] and manganese in nitric and hydrochloric acids[98] have been determined by irradiating the residue after evaporation. Sodium and phosphorus have been determined in cervical mucus which has been dried and ashed.[99] Similar analyses have been reported for vanadium, arsenic, molybdenum, tungsten, rhenium and gold in dried marine organisms[100,101] and for gold in wine.[102]

Simple freeze-drying has been utilized to reduce sample size and to prevent the radiolysis of water present in a sample. Such a procedure facilitated the determination of selenium in eye lenses,[103] egg yolks[104] and sera and plasma,[105] of cadmium in biological tissue[106] and of bromine, chlorine, radium, mercury, chromium, phosphorus, rubidium, iron, cobalt and zinc in blood.[107] Freeze-drying has also been used as a final preconcentration step before irradiation of effluents from gel permeation[61] and ion-exchange chromatography[16] as cited above.

The methods of drying and ashing have certain disadvantages associated with their use. A sample, for example, may contain a species of interest that will volatilize during the drying or ashing process. A case in point is the determination of mercury and its compounds.[93] A recent paper,[72] however, reported a way to circumvent this problem. The procedure entailed the freeze-drying of an aqueous sample in a flask lined with a plastic film. The film itself was a convenient matrix for sample irradiation and good recovery of the mercury was reported as a result of the reaction of mercuric ion with unsaturated bonds present in the plastic film. Other problems associated with drying and ashing methods are cited in a paper describing the determination of several elements in sea-water.[93] Poor results were attributed to a combination of adsorption on storage container walls, interference from sodium and chloride gamma-spectra, and too rapid decay of short-lived nuclides.

ELECTROCHEMICAL METHODS

Electro-deposition is a very convenient way to concentrate trace metals for analysis. It offers the advantage of yielding a chemically and physically inert sample on a relatively small surface area that is suitable for analysis. Lux[108,109] initiated the idea of electrochemical preconcentration by the electrodeposition of silver on a rotating platinum disc electrode from a solution which also contained large amounts of cadmium. The deposited silver was irradiated and dissolved in *aqua regia* and a gamma-spectrum of the solution was taken. Direct counting of the silver film on the platinum electrode was not feasible, owing to the high background activity of the platinum itself. A relatively high background activity was also noted for the dissolved sample, owing to dissolution of some of the active platinum.

The problems associated with the use of a platinum substrate in NAA can be eliminated by choosing an electrode material that will not give rise to large interfering activity on irradiation. Such an approach was taken by Sion *et al.*[29] who determined mercury in aqueous solutions by electro-depositing it on aluminium wire. Since aluminium has a very short half-life, the electrode and deposited film could be irradiated directly and after approximately 30 min the mercury activity could be counted without background interference.

Pyrolytic graphite has also been used as an electrode material. Since pyrolytic graphite is totally carbon, it is not activated to yield a gamma-emitting isotope,[59] and since it can be obtained in a very pure form,[110] this substrate produces a very low background activity without any post-irradiation waiting period. Thus, counting can begin immediately after irradiation and even short-lived nuclides can be determined on this substrate. Several accounts of the application of this material to NAA have been published.[6,30–32,111–115]

MISCELLANEOUS METHODS

Other preconcentration techniques have also been reported. Sion *et al.*[29] have amalgamated mercury present in aqueous solutions on aluminium powder by stirring the powder in contact with the solution for several hours. After equilibrium has been achieved, the powder is filtered, dried and irradiated. After a brief waiting period, the activity of the aluminium declines and the mercury activity can be counted.

Total blood iodine[116] and protein bound iodine in serum[12] have been determined by NAA after oxidation of the sample and distillation from phosphoric acid solutions.

In biological materials the greatest potential interference for the NAA determination of trace metals is the presence of large amounts of sodium, potassium, chloride and bromide ions in the sample. These ions can be removed to an appreciable extent by dialysis of the sample. While heavy metals are usually complexed in biological materials, the uncomplexed interfering ions diffuse through the dialysis membrane, leaving the organically-bound heavy metals in the sample, which can then be irradiated. This technique has been used in the determination of manganese and copper in blood serum and cerebrospinal fluid,[117] protein-bound selenium in blood,[118] and brominated protein in serum.[119] Human serum has been dialysed before ion-exchange separation and irradiation for the determination of free thyroxine.[14]

Zusammenfassung—Es wird eine Übersicht über die Methoden gegeben, die zur Anreicherung von Spurenelementen in Proben für die Neutronenaktivierungsanalyse vorgeschlagen wurden. Der Nachdruck liegt auf der Klassifizierung der Methoden; praktische Beispiele dienen zur Illustration.

Résumé—On présente une revue des méthodes qui ont été proposées pour l'enrichissement d'éléments à l'état de traces dans des échantillons qui doivent être analysés par les méthodes par activation de neutrons. On insiste sur la classification des méthodes, avec illustrations complètes au moyen d'exemples pratiques.

REFERENCES

1. H. J. M. Bowen and D. Gibbons, *Radioactivation Analysis*, Clarendon Press, Oxford, 1963.
2. G. W. Leddicotte and S. A. Reynolds, *The Determination of Trace Elements by Neutron Radioactivation Analysis*, ASTM Bulletin, 1953, 29.
3. H. P. Yule, *Anal. Chem.*, 1965, **37**, 129.
4. A. A. Smales, in *Trace Analysis*, J. H. Yoe and H. J. Koch, Jr., eds., p. 518. Wiley, New York, 1957.
5. G. T. Seaborg and J. J. Livingood, *J. Am. Chem. Soc.*, 1938, **60**, 1784.
6. H. B. Mark, Jr., *J. Pharm. Belg.*, 1970, **25**, 367.
7. F. Girardi, *Talanta*, 1965, **12**, 1017.
8. D. M. Taylor, *Nucl. Activ. Tech. Life Sci., Proc. Symp.*, Amsterdam, 1967, p. 391.
9. T. Joyner, M. L. Heally, D. Chakrovarti and T. Koyanagi, *Environ. Sci. Technol.*, 1967, **1**, 417
10. E. M. Smith, J. M. Mozley and H. N. Wagner, Jr., *J. Nucl. Med.*, 1964, **5**, 828.
11. C. W. Tang and R. H. Tomlinson, *Nucl. Activ. Tech. Life Sci., Proc. Symp.*, Amsterdam, 1967, p. 427.
12. S. Hamada, K. Torizuka, K. Hamamoto, J. Nakagawa, T. Mori, R. Morita, T. Nakagawa, J. Kanishi, T. Miyake and M. Fukare, *Radioisotopes*, 1967, **16**, 14.
13. R. H. Tomlinson and M. W. Billingshurst, *Trans. Am. Nucl. Soc.*, 1969, **12**, 458.
14. S. Hamada, K. Torizuka, K. Hamamoto, T. Mori, R. Morita, T. Nakagawa and J. Kanishi, *Radioisotopes*, 1969, **18**, 354.
15. M. H. Feldman, J. McNamara, R. C. Rebra and W. Webster, *J. Nucl. Med.*, 1967, **8**, 123.
16. V. E. Zaichik, Y. Ryabukhin, A. D. Mel'nik and V. Cherkashin, *Med. Radiol.*, 1970, **15**, 33.
17. H. N. Wagner, Jr., W. B. Nelp and J. H. Dowling, *J. Clin. Invest.*, 1961, **40**, 1984.
18. D. J. Morgan, A. Black and G. R. Mitchell, *Analyst*, 1970, **94**, 740.
19. S. Ohno, M. Suzuki, K. Sasajima and S. Iwata, *ibid.*, 1970, **95**, 260.
20. G. J. Olivares, L. Aronow and F. Kendel-Vegas, *Acta Cient. Venez.*, 1967, **18**, 9.
21. A. A. Smales and L. Salmon, *Analyst*, 1955, **80**, 37.
22. K. D. Linstedt and P. Kruger, *J. Am. Water Works Assoc.*, 1969, **61**, 85.
23. *Idem, Anal. Chem.*, 1970, **42**, 113.
24. J. A. Warburton and L. G. Young, *J. Appl. Meteorol.*, 1968, **7**, 433.
25. H. G. Meyer, H. J. Born, H. Stärk and C. Turkowsky, *Radiochim. Acta.*, 1968, **10**, 128.
26. A. D. Matthews and J. P. Riley, *Anal. Chim. Acta*, 1970, **51**, 455.
27. V. Maxia, *Ric. Sci.*, 1959, **29**, 1476.
28. F. W. Lima and C. M. Silva, *J. Radioanal. Chem.*, 1968, **1**, 147.
29. H. Sion, J. Hoste and J. Gillis, *Microchem. J. Symp. Ser.*, 1962, **2**, 959.
30. U. Eisner, J. M. Rottschafer, F. J. Berlandi and H. B. Mark, Jr., *Anal. Chem.*, 1967, **39**, 1466.

31. U. Eisner and H. B. Mark, Jr., *Talanta*, 1969, **16**, 27.
32. H. B. Mark, Jr., U. Eisner, J. M. Rottschafer, F. J. Berlandi and J. S. Mattson, *Environ. Sci. Technol.*, 1969, **3**, 165.
33. T. E. Green, S. L. Law and W. J. Campbell, *Anal. Chem.*, 1970, **42**, 1749.
34. A. A. Benson, B. Marvo, R. J. Flipse, H. W. Yurrow and W. W. Miller, *Proc. 2nd. Int. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, paper 858.
35. F. Nakayama and R. Blomstrand, *Acta Chem. Scand.*, 1961, **15**, 1595.
36. R. Blomstrand and K. Nakayama, *Scand. J. Clin. Lab. Invest.*, 1962, **14**, 28.
37. *Idem, J. Neurochem.*, 1961, **8**, 230.
38. E. H. Strickland and A. A. Benson, *Arch. Biochem. Biophys.*, 1960, **88**, 344.
39. D. C. Shaw, *Nature*, 1967, **215**, 410.
40. G. W. Rushinzky and W. W. Miller, *Anal. Biochem.*, 1967, **20**, 181.
41. J. Lustinec, *Biol. Plant. Acad. Sci. Bohemoslov.*, 1960, **2**, 67.
42. K. Schmeiser and D. Jerchel, *Angew. Chem.*, 1953, **65**, 366.
43. *Idem, ibid.*, 1953, **65**, 490.
44. W. A. Skinner, M. A. Leaffer and R. M. Parkhurst, *J. Pharm. Sci.*, 1968, **57**, 338.
45. A. Dimitriadou, P. C. R. Turner and T. R. Fraser, *Nature*, 1963, **197**, 446.
46. R. P. Ouellette, J. F. Balcius and K. Zappinger, *Intern. J. Appl. Radiat. Isotop.*, 1966, **17**, 649
47. I. Yanagisawa and H. Yoshikawa, *Radioisotopes*, 1967, **16**, 554.
48. F. P. W. Winteringham, A. Harrison and R. G. Bridges, *Nature*, 1951, **167**, 106.
49. *Idem, Nucleonics*, 1952, **10**, 52.
50. H. J. Born and H. Stärk, *Atomkernenergie*, 1959, **4**, 286.
51. F. Baumgartner and A. Schon., *J. Chromatog.*, 1964, **13**, 266.
52. J. M. Steim and A. A. Benson, *Anal. Biochem.*, 1964, **9**, 21.
53. A. J. Barak and S. C. Swanberg, *J. Chromatog.*, 1967, **31**, 282.
54. T. Nascutiu, *Aced. Rep. Populare Romine, Studii Cercetoni Chim.*, 1962, **10**, 275.
55. *Idem, Rev. Roumaine Chim.*, 1964, **9**, 283.
56. L. T. Harmison, S. Lakshmanan and D. Duffey, *Trans. Am. Nucl. Soc.*, 1965, **8**, 86.
57. J. B. Smathers, D. Duffey and S. Lakshmanan, *Anal. Chim. Acta*, 1969, **46**, 9.
58. *Idem, Nucl. Appl. Technol.*, 1969, **7**, 84.
59. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, New York, 1967.
60. H. Seiler, *Helv. Chim. Acta.*, 1970, **53**, 1893.
61. K. Fritze and R. Robertson, *J. Radioanal. Chem.*, 1968, **1**, 463.
62. D. J. R. Evans and F. Klaus, *Anal. Chim. Acta*, 1969, **44**, 1.
63. J. C. Veselsky, M. Nedbalek and O. Suschny, *Intern. J. Appl. Radiat. Isotop.*, 1970, **21**, 225.
64. H. R. Lukens, K. Heydorn and T. Choy, *Trans. Am. Nucl. Soc.*, 1965, **8**, 331.
65. K. Heydorn and H. R. Lukens, *Danish AEC Riso Report* No. 138, 1966.
66. M. C. Haven, G. T. Haven and A. L. Dunn, *Anal. Chem.*, 1966, **38**, 141.
67. O. Veveris, S. H. Mihelson, Z. Pelekis, L. Pelekis and J. Toure, *Latv. PSR Zinat. Akad. Vestis. Fiz. Teh. Zinat. Ser.*, 1969, **2**, 25.
68. J. F. Slowey, D. Hedges and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-22660, 1960.
69. J. F. Slowey, *U.S. At. Energy Comm. Rept.*, TID-233295 Sect. 2, 1966.
70. J. C. White and W. S. Lyon, *Talanta*, 1965, **12**, 823.
71. R. Bock and B. Jost, *Z. Anal. Chem.*, 1970, **250**, 358.
72. J. G. Montalvo, Jr., D. P. Thibodeaux and E. Klein, *Anal. Chim. Acta*, 1970, **52**, 160.
73. S. T. Hirozawa, personal communication, 1970.
74. H. Marchant and F. Hecht, *Monatsh. Chem.*, 1964, **95**, 742.
75. E. Rona, D. W. Hood, L. Muse and B. Buglio, *Limnol. Oceanog.*, 1962, **7**, 201.
76. B. W. Dixon, J. F. Slowey and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-23295 Sect. 3, 1966.
77. D. W. Hayes, J. F. Slowey and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-23295 Sect. 4, 1966.
78. O. T. Høgdahl, *NATO Research Grant* #203, Semiannual Progress Report #2, Oct. 1, 1965–Mar. 31, 1966.
79. *Idem, ibid.*, #4, Oct. 1, 1966–Mar. 31, 1967.
80. O. T. Høgdahl, S. Melson and V. T. Bowen, *Neutron Activation Analysis of Lanthanide Elements in Sea Water*, Advances in Chemistry Series #73, p. 308. R. F. Gould, Ed., American Chemical Society Publications, 1968.
81. H. Hamaguchi, R. Kuroda, R. Hoshara and T. Shimizu, *Nippon Genshiryoku Gakkaishi*, 1963, **5**, 662.
82. M. Osawa, O. Tokunaga, M. Itani and M. Sakanoue, *J. Nucl. Sci. Technol.*, 1966, **3**, 333.
83. K. S. Bhatki and A. N. Dingle, *Radiochem. Radioanal. Lett.*, 1970, **3**, 71.

84. G. E. Harrison and W. H. A. Raymond, *J. Nucl. Energy*, 1955, **1**, 290.
85. S. R. Rao, A. A. Khan and P. R. Kamath, *Nucl. Radiation Chem. Proc. Symp., Bombay*, 1964, p. 199.
86. T. Oda, *Radioisotopes*, 1969, **18**, 39.
87. G. R. Doshi, *Indian J. Chem.*, 1967, **5**, 580.
88. B. L. Twitty and M. W. Boback, *Anal. Chim. Acta*, 1970, **49**, 19.
89. H. Wiechen, *Milchwissenschaft*, 1970, **25**, 95.
90. W. H. Ellis, G. J. Fritz and G. G. Rocco, *Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis*, p. 248. Texas A and M Press, College Station, Texas, 1966.
91. J. Selz, W. Haerdi and D. Monnier, *Chimia*, 1963, **17**, 354.
92. A. Wyttenbach, *ibid.*, 1966, **20**, 119.
93. D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta*, 1965, **29**, 259.
94. D. Z. Piper and G. G. Goles, *Anal. Chim. Acta*, 1969, **47**, 560.
95. L. M. Mosulishvili, N. E. Kuchava and E. N. Ginturi, *Soobshch. Akad. Nauk. Gruz. SSR*, 1970, **59**, 93.
96. G. Schmidt, *Kernforschungzentrum Rept.*, KFK-863, 1968.
97. J. F. Emery and G. W. Leddicotte, *U.S. At. Energy Comm. Rept.*, CF-58-9-20, 1960.
98. W. Otwinowski and Z. Allina, *Nukleonika*, 1963, **8**, 411.
99. E. Odelblad, B. Westin and K. G. Malmfors, *Acta Radiol.*, 1958, **49**, 137.
100. R. Fukai and W. W. Meinke, *Nature*, 1959, **184**, 815.
101. *Idem Limnol. Oceanog.*, 1962, **7**, 186.
102. G. I. Beridze, G. R. Macharoshvili and L. M. Mosulishvili, *Radiokhimiya*, 1969, **11**, 726.
103. R. H. Filby and W. L. Yakely, *Radiochem. Radioanal. Lett.*, 1969, **2**, 307.
104. J. Cals, *Mater. Respub. Konf. Probl. "Mikroelem. Med. Zhivotnovod."*, *1st.*, 1968, M. Kruming, ed., p. 170. Baku, USSR, 1969.
105. B. Maziere, D. Comar and C. Kellershohn, *Bull. Soc. Chim. Fr.*, 1970, 3767.
106. K. W. Lieberman and H. H. Kramer, *Anal. Chem.* 1970, **42**, 266.
107. W. A. Haller, R. H. Filby and L. A. Rancitelli, *Nucl. Appl.*, 1969, **6**, 365.
108. F. Lux, *Radiochim. Acta*, 1962, **1**, 20.
109. *Idem*, *ibid.*, 1964, **3**, 50.
110. *General Electric Pyrolytic Graphite Engineering Handbook*, General Electric Corporation, Detroit, 1963.
111. H. B. Mark, Jr., and F. J. Berlandi, *Anal. Chem.*, 1964, **36**, 2062.
112. B. H. Vassos, F. J. Berlandi, T. E. Neal and H. B. Mark, Jr., *ibid.*, 1965, **37**, 1653.
113. B. H. Vassos, *Ph.D. Thesis*, University of Michigan, 1965.
114. H. B. Mark, Jr., F. J. Berlandi, B. H. Vassos and T. E. Neal. *Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis*, p. 107. Texas A and M Press, College Station, Texas, 1966.
115. F. J. Berlandi, *Ph.D. Thesis*, University of Michigan, 1966.
116. C. Kellershohn, D. Comar and C. Lepoec, *Intern. J. Appl. Radiat. Isotop.*, 1961, **12**, 87.
117. E. L. Kanobrocki, T. Fields, C. F. Decker, L. F. Case, E. B. Miller, E. Kaplan and Y. T. Oester, *ibid.*, 1964, **15**, 175.
118. R. H. Tomlinson and R. C. Dickson, *Proc. 1965 Intern. Conf. Modern. Trends in Activation Analysis*, p. 66. Texas A and M Press, College Station, Texas, 1966.