14 June 1974, Volume 184, Number 4142 SCIENCE

Recent Developments in the Analysis of Toxic Elements

New methodology has made possible the determination of trace concentrations of many toxic elements.

Donald J. Lisk

The recent discovery of ubiquitous environmental contamination by mercury has now caused much concern about the possible presence of many other toxic elements in biological and geochemical systems (*1*). Even the rare-earth elements have been reported at astonishingly elevated concentrations in aquatic plants (*2*). Fortunately, the concurrent development of new and improved analytical methodology has made it possible to study and monitor these elements at extreme trace concentrations. It is my purpose in this article to survey some of the recent analytical advances and their practical applications to biological problems.

Sample Ashing, Element Isolation, and Concentration

Although perhaps the least glamorous, the initial steps in trace element analysis, namely, reagent purification, sample preparation and ashing, and element isolation and concentration, are usually the most crucial. Excellent publications dealing with these steps are those of Mizuike (*3*), Tölg (*4*), and Gorsuch (*5*). Gorsuch deals comprehensively with sample ashing, presenting data, element by element, on recovery and loss for different ashing procedures, temperatures, and operating parameters. Mizuike and Tölg discuss ashing procedures, including dry and wet, oxygen flask combustion, and oxygen bomb, oxygen stream, and low-temperature activated oxygen techniques. They explain errors attributable to laboratory and reagent contamination and to adsorption and vaporization losses, and discuss remedial measures. Separations based on vaporization, liquid-liquid extraction, precipitation, electrodeposition, ion exchange, and other methods are reviewed.

Recent devices (*6*) for the rapid ashing of inorganic or organic samples consist of a Teflon-lined steel vessel into which the sample and oxidizing acid are introduced. Heat applied to the sealed container results in the rapid decomposition and solution of the sample. Acid decomposition of samples under pressure in plastic bottles has been reported (*7*). A simple apparatus has recently been described (*8*) for the extremely rapid oxidation of plant material in generated nitric acid vapor prior to metal analysis. Rapid sample solution in soluene, a quaternary ammonium hydroxide, has been described (*9*). Oxygen flask combustion is still an effective and rapid method of sample decomposition for use prior to the determination of volatile elements such as mercury (*10*) or selenium (*11*). It can be particularly advantageous for the combustion of biological materials which may contain an element in more than one valence state such as trivalent and pentavalent arsenic, the former being more volatile and easily lost. Its restriction to the combustion of dried samples no larger than 1 to 2 grams may no longer be a limitation, owing to the improvement in the attainable element detection limits of several new methods. A paper by Katz (*12*) provides a useful summary of references dealing with solvent extraction for the isolation of metals.

Analytical Instrumentation

For convenience, I shall discuss the various analytical techniques in alphabetical order. Anodic stripping voltammetry, especially with differential pulsing (*13*), is a versatile and extremely sensitive technique for the detection of metals at concentrations reportedly down to 0.01 part per billion. If ever a method was peculiarly suited for a specific sample matrix, it would be the application of this technique to studying the chemistry of ultratrace concentrations of metals in aquatic systems. Consecutive multimetal analysis in the same solution is possible, and the technique is applicable to a broad range of elements. It is particularly advantageous in aquatic investigations since it can be easily used to determine the proportion of the free element present and also the proportion complexed as well as the rate of complexation of an added ion (*14*). The determination of metals in natural waters can be strongly dependent on *p*H. To obviate the introduction of reagent impurities a system was recently developed (*15*) in which *p*H can be controlled over a range of three or four units by replacing the typical inert purging gas with a mixture of carbon dioxide and nitrogen in specific proportions depending on the *p*H desired. Anodic stripping methods have been applied to the determination of several toxic metals in airborne particulates (*16*) and in tissue, blood, urine, and hair (*17*).

Conventional flame atomic absorption spectrophotometry has been amply reviewed (*18*). Reports dealing with

The author is professor of pesticide chemistry and director of the Pesticide Residue Laboratory, Food Science Department, Cornell University, Ithaca, New York 14850.

the sampling boat technique (*19*), interferences (*20*), and biological applications (*21*) have appeared. Among the most recent developments in the field of trace element analysis are the "flameless" atomic absorption methods. This technique, requiring only milligram amounts of sample, is extremely sensitive and applicable to the determination of perhaps 60 elements. Like anodic stripping voltammetry, this technique appears to be uniquely suited to biological problems where sample size is very limited, for example, the extent of absorption of cadmium by a single mouse kidney. Its application to the analysis of a tiny subsample demands thorough preliminary sample mixing, however. A number of atomizer designs have emerged (*22*). The use of the method for element analysis in biological samples has truly mushroomed in the past 2 years (*23*). The well-known technique (*24*) of the preliminary reduction of mercuric ion to mercury vapor followed by circulation through an atomic absorption light path is another form of flameless atomic absorption analysis. Direct volatilization into an atomic absorption flame of elements such as arsenic, antimony, and selenium by prior chemical reduction to their respective gaseous hydrides now makes possible a rapid, sensitive analysis of these elements (*25, 26*). This is especially true when electrodeless discharge lamps are used as intense sources in place of hollow cathode lamps (*27*). A comparison of the advantages of atomic absorption and atomic fluorescence (*28*) for metal analysis has been carried out by Kahn (*29*).

The effective application of emission spectroscopy methods to the multimetal analysis of biological materials has been reported (*2, 30*). A recent development which significantly enhances the signal-to-noise ratio and the limit of detection of emission methods is the argon plasma source now commercially available as the "Spectra Jet" (*31*). Quantities ranging from 0.05 to 35 nanograms are reportedly detectable for 35 elements. Its successful application to the analyses of a range of elements requires a highly resolving monochrometer. As reported above for atomic absorption, traces of arsenic and antimony have been determined by volatilizing their gaseous hydrides into a source consisting of an electrical discharge in argon and measuring their spectral emission lines (*32*). A very promising and specific method involves the use of the microwave-powered emission detector (*33*) for the analysis of nanogram quantities of volatile metal chelates separated by gas chromatography (*34*). Sample size must be kept small, especially with refractory elements, to obviate the condensation of metals in the discharge tube. The entire gas chromatography and detection system is now commercially available from Applied Research Laboratories, Ltd. Laser excitation has also been used to quantitatively measure trace metals by emission spectrography (*35*).

Gas chromatography has been extensively investigated for trace metal analysis. A method involving the preparation of volatile fluoroacetylacetonates of metals which are then chromatographed and detected by electron capture techniques offers unparalleled sensitivity in many instances. Fluorinated acetylacetonates of aluminum, beryllium, chromium, iron, and rhodium have been determined by this scheme with sensitivities down to 10^{-13} gram (*36*). Hexafluoromonothioacetylacetone is a new liquid that can be used for the preparation of volatile chelates of divalent metals including copper, zinc, nickel, cadmium, and lead (*37*). The factors that influence the volatility of metal fluoroacetylacetonates have been discussed (*38*). A hydrogen-rich flame ionization detector has been used to detect organometallic compounds of iron, lead, and tin in the range from 10 to 30 picograms (*39*). Organometallic compounds containing nickel, mercury, lead, copper, tin, and other elements have been determined in gas chromatographic effluents by the use of a flame photometric detector (*40*). In a sensitive method for the analysis of selenium in seawater the 5-nitropiaselenol derivative is detected by electron-capture gas chromatography (*41*). Careful attention must be given to proper column operating parameters and conditioning for the successful chromatography of metal chelates. Even thin-layer chromatography has been employed for the separation of 20 elements as chelates (*42*).

For characterization and sensitive element analysis of sample surfaces in situ, the laser (*43, 44*), electron (*45*), and ion (*46, 47*) microprobe techniques are most valuable. These instruments which, respectively, produce light emission of sample elements by laser excitation, x-ray emission of sample elements by electron bombardment, or charged ions by ion bombardment have progressively improved. The attainable detection limits of the three techniques are, respectively, 10^{-15}, 10^{-17}, and 10^{-19} gram (*44*). Detectable element concentration necessarily must increase as the specimen area being bombarded becomes smaller. Geochemical (*47*) and biological (*45*) applications of the techniques have been described.

The essentials of the method of neutron activation analysis, not a new technique, have been well described (*48*). Its recent use for the sensitive simultaneous analysis of some 60 elements in a sample is finding many applications. In this method the dry unashed sample is directly irradiated in a nuclear reactor for both short (minutes) followed by longer (hours) periods. Gamma-ray spectra are then obtained after decay times ranging from minutes to several days after the irradiation. Gamma-ray photopeaks in the pulse height spectra are then identified and quantitatively determined by means of a multichannel analyzer and a computer. The principal advantages of the method are its sensitivity, the spectrum of elements detectable, and the elimination of external contamination owing to nondestructive analysis. The incorporation of a new low-energy photon detector (*49*) should increase the accuracy of the technique as a result of its sensitivity to low-energy photons and its fine resolving ability. New methods of separating sample elements prior to neutron activation analysis have been reported (*50*), and a review of preliminary methods used to increase element concentration has appeared (*51*). Neutron activation has been applied to a number of biological and environmental problems (*52*). However, the fact that this technique cannot be used to determine certain important elements such as lead is a limitation.

Pulse polarographic methods, especially the differential pulse technique, are significantly more sensitive than conventional polarography (*53, 54*). In the latter technique a slow direct-current ramp voltage is applied to the dropping mercury electrode. During the life of each mercury drop a small voltage pulse is applied for about 50 milliseconds. The current is measured just before and again near the end of the pulse. During the two measurements the charging current background decreases to a negligible value. If the difference between the two current measurements is recorded, much greater signal-to-noise response is achieved since mainly the Faradaic current is being sensed. Ele-

ment concentrations of $10^{-8}M$ can therefore often be measured. Instrumental artifacts caused by variable scan rates, drop times, and pulse amplitudes have been described as well as the means of optimizing peak current and shortening analysis time (*55*). The differential pulse method has been applied to the analysis of environmental samples (*53*).

Spark-source mass spectrometry is another powerful tool for ultratrace multielement analysis (*56*). In principle it involves the production of ions in an ashed sample located between electrodes with high voltage excitation. The ions with a high kinetic energy spread are first energy-focused in an electrostatic analyzer. The ions then enter a magnetic field and finally impinge upon a photographic plate at different points depending on their mass-to-charge ratio. Depending on the accuracy desired, analysis may be carried out by referring the intensity of the desired element line to (i) that of an internal matrix element line, (ii) that of the same line in a series of known standards, or (iii) that of an added isotope of the element. More recently, electrical detection methods have been used in which all ion species are scanned across a collector slit comprising the principal focus, or individual element isotopes may be examined by electrostatic peak-switching with static integration (*57*). Most attractive is the very recent computer interfacing of electrically recorded spectra which automatically corrects and interprets the spectra of all elements, thus greatly simplifying and speeding the analysis (*58*). The advantages of spark-source mass spectrometry are high sensitivity, comprehensive element coverage, and rapid analysis. The technique has found extensive use in biological, environmental, and forensic applications (*59*).

Finally, x-ray spectrometric methods useful for single or multielement analysis have greatly advanced. In the more conventional wavelength-dispersive mode the sample is directly irradiated by an x-ray source, and the stimulated secondary emission is resolved by the use of a crystal goniometer prior to detection. Although this method provides unparalleled resolution, considerable signal intensity is lost through absorption in the crystal and, as a result, the sensitivity is reduced. In a new modification, the energy-dispersive x-ray method (*60*), the sample is irradiated and the secondary x-rays directly enter a multichannel analyzer for resolution

Table 1. References to methods of trace element analysis in biological samples. Samples: a, air; at, animal tissue; bl, blood; bm, biological material; f, fish; fd, food; m, milk; p, plant material; pm, plasma; r, rock; s, serum; sl, soil; u, urine; and w, water. Methods: AA, atomic absorption; ASV, anodic stripping voltammetry; Color., colorimetry; Emiss., emission spectrometry; Fluor., fluorescence analysis; GLC, gas-liquid chromatography; NAA, neutron activation analysis; and Polar., polarography.

Element	Sample	Method	Reference
Arsenic	at	Color.	(*67*)
Arsenic		AA	(*25*)
Arsenic		Polar.	(*68*)
Antimony	w	ASV	(*69*)
Antimony		AA	(*70*)
Barium		AA	(*71*)
Barium		Emiss.	(*71*)
Beryllium	r	AA	(*72*)
Beryllium	u	GLC	(*73*)
Beryllium	bm	AA	(*74*)
Beryllium		AA	(*75*)
Beryllium	a	GLC	(*76*)
Beryllium	r	GLC	(*77*)
Beryllium		GLC	(*78*)
Beryllium	bm	GLC	(*79*)
Bismuth	w	ASV	(*69*)
Cadmium	fd	Polar.	(*80*)
Cadmium	bm	AA	(*81*)
Cadmium	fd	AA	(*82*)
Cadmium	bm	AA	(*83*)
Chromium	u	AA	(*84*)
Chromium	bm	AA	(*85*)
Chromium	u	AA	(*86*)
Chromium	bm	AA	(*87*)
Chromium	bm	Emiss.	(*88*)
Chromium	s	GLC	(*89*)
Chromium	bm	GLC	(*90*)
Chromium	pm	GLC	(*91*)
Cobalt	sl	NAA	(*92*)
Cobalt	bm	AA	(*93*)
Cobalt	p	AA	(*94*)
Copper		AA	(*95*)
Copper	m	AA	(*96*)
Copper	at	AA	(*97*)
Copper	s	AA	(*98*)
Copper	bm	AA	(*99*)
Copper	fd	AA	(*100*)
Copper	u	AA	(*101*)
Copper	sl	Color.	(*102*)
Gold	r	AA	(*103*)
Gold	s	AA	(*104*)
Gold	bl	AA	(*104*)
Gold	u	AA	(*104*)
Gold		AA	(*105*)
Gold		AA	(*106*)
Lead	bl	AA	(*107*)
Lead	a	AA	(*108*)
Lead	bl	AA	(*109*)
Lead	f	AA	(*110*)
Lead	bl	AA	(*111*)
Lead	bl	AA	(*112*)
Lead	bl	AA	(*113*)
Lead	u	AA	(*114*)
Lead	bm	Color.	(*115*)
Lead	bl	Color.	(*116*)
Lead	f	Polar.	(*117*)
Lead	f	Polar.	(*118*)
Lead	f	AA	(*117*)
Lead	f	AA	(*118*)
Lead	p	AA	(*119*)
Lead	a	AA	(*120*)
Lead	bl	AA	(*121*)
Lead	bm	AA	(*122*)
Lead	bl	AA	(*123*)
Lead	bl,u	AA	(*124*)
Lead	bl,u	AA	(*125*)
Lead	bl	AA	(*126*)
Lead	bl	AA	(*127*)
Lead	m	AA	(*128*)
Lead	bl	AA	(*129*)
Lead		AA	(*130*)
Lead	a	AA	(*131*)
Lead	bl	AA	(*109*)
Lead	bl,u	ASV	(*132*)
Lithium	s,u	AA	(*133*)
Manganese	bl	AA	(*134*)
Mercury	p	Color.	(*10*)
Mercury	f	AA	(*135*)
Mercury	bm	AA	(*136*)
Mercury	u	Color.	(*137*)
Mercury		AA	(*138*)
Mercury		AA	(*139*)
Mercury	bm	AA	(*140*)
Mercury	bm	AA	(*141*)
Mercury	bm	NAA	(*142*)
Mercury	bm	NAA	(*143*)
Mercury		NAA	(*144*)
Mercury	bm	NAA	(*145*)
Mercury	bm	NAA	(*146*)
Mercury	sl	NAA	(*147*)
Mercury	sl	AA	(*147*)
Mercury	w	AA	(*148*)
Mercury	a	AA	(*149*)
Mercury		AA	(*150*)
Mercury	f	Color.	(*151*)
Methylmercury	bm	GLC	(*152*)
Methylmercury	bm	GLC	(*153*)
Methylmercury	fd	GLC	(*154*)
Methylmercury	fd,f	GLC	(*155*)
Methylmercury	f	GLC	(*156*)
Methylmercury	bm	AA	(*157*)
Methylmercury	u,bl	Color.	(*158*)
Methylmercury		GLC	(*159*)
Methylmercury	f	GLC	(*160*)
Methylmercury	bl	AA	(*161*)
Methylmercury	f	GLC	(*162*)
Methylmercury	bm	GLC	(*163*)
Molybdenum	p	Color.	(*164*)
Molybdenum	w	AA	(*165*)
Nickel		AA	(*95*)
Nickel	fd	GLC	(*166*)
Selenium	w	AA	(*167*)
Selenium		AA	(*168*)
Selenium	bm	Fluor.	(*169*)
Selenium	p	Color.	(*11*)
Selenium	bm	Fluor.	(*170*)
Selenium	s	NAA	(*171*)
Selenium	w	GLC	(*41*)
Silver	w	AA	(*172*)
Silver	r	AA	(*173*)
Strontium	bl	AA	(*134*)
Tin	fd	AA	(*174*)
Tin	bm	NAA	(*175*)
Tin	r,sl	Color.	(*176*)
Thallium	u	AA	(*177*)
Vanadium	r	AA	(*178*)
Vanadium	bm	Color.	(*179*)
Zinc	w	NAA	(*180*)
Zinc		AA	(*181*)
Zirconium	bm	AA	(*182*)

and detection. The system has been computerized, which permits the simultaneous analysis of about 50 elements. Various computer programs are necessary to correct for interelement enhancement and absorption, and the final data are printed out showing each elemental symbol and the corresponding concentration. Detection limits range down to 1 part per million or less. X-ray methods have been applied to the elemental analysis of air particulates (*61*), lake sediments (*62*), aquatic plants (*2*), urine (*63*), and other materials (*64*). Another interesting development is heavy ion–induced x-ray fluorescence (*65*). Excitation with a heavy ion beam reduces bremsstrahlung background, and the sensitivity improves up to several hundredfold, or 10^{-15} gram per square centimeter. This method has been applied to the analysis of elements in air pollutants (*65*) and blood (*66*).

Analytical Methods for Specific Elements

The application of much of the instrumentation described above to biological and environmental problems has been rapid. Table 1 lists references to methods of analysis of traces of specific elements in designated samples. Where appropriate, older colorimetric or fluorescent techniques are also cited since they are still reliable and often sufficiently sensitive and the instrumentation is frequently found in most laboratories.

Conclusions

One may conclude that it is impractical to confine oneself to any one analytical method since ever more sensitive instrumentation continues to be produced. However, in certain methods such as anodic stripping voltammetry and flameless atomic absorption it may be background contamination from reagent impurities and surroundings rather than instrument sensitivity which controls the limits of element detection. The problem of contamination from dust or glassware is greatly magnified when the sample size becomes ever smaller. Air entering laboratories near highways may contain trace quantities of lead, cadmium, barium, antimony, and other elements from engine exhaust. Even plastic materials contacting the sample may be suspect as a source of contamination since specific metals may be used as catalysts in the synthesis of the plastic and traces may be retained in it. Certain elements may even be deliberately added to plastics during manufacture for identification purposes. Nondestructive methods such as neutron activation and x-ray techniques thus offer great advantages not only in time but in the elimination of impurities introduced during sample ashing. Future improvements in attainable limits of detection may arise largely from progress in the ultrapurification of reagents and "clean-room" techniques. Finally, the competence of the analyst is also vitally important in the skillful operation of modern complex analytical instrumentation and in the experienced evaluation of data.

References

1. D. J. Lisk, *Adv. Agron.* **24**, 267 (1972).
2. U. M. Cowgill, *Appl. Spectrosc.* **27**, 5 (1973).
3. A. Mizuike, in *Trace Analysis: Physical Methods*, G. H. Morrison, Ed. (Interscience, New York, 1965), pp. 103–159.
4. G. Tölg, *Talanta* **19**, 1489 (1972).
5. T. T. Gorsuch, *The Destruction of Organic Matter* (Pergamon, New York, 1970).
6. B. Bernas, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1973), p. 41; P. E. Paus, *At. Absorpt. Newsl.* **10**, 44 (1971).
7. W. J. Adrian, *At. Absorpt. Newsl.* **10**, 96 (1971).
8. A. D. Thomas and L. E. Smythe, *Talanta* **20**, 469 (1973).
9. A. S. Jackson, L. M. Michael, H. S. Schumacher, *Anal. Chem.* **44**, 1064 (1972).
10. W. H. Gutenmann and D. J. Lisk, *J. Agric. Food Chem.* **8**, 306 (1960).
11. ———, *ibid.* **9**, 488 (1961).
12. S. A. Katz, *Am. Lab (Greens Farms, Conn.)* (Oct. 1972), p. 19.
13. H. Siegermann and G. O'Dom, *ibid.* (June 1972), p. 59.
14. H. E. Allen, W. R. Matson, K. H. Mancy, *J. Water Pollut. Control Fed.* **42**, 573 (1970).
15. A. Zirino and M. L. Healy, *Environ. Sci. Technol.* **6**, 243 (1972).
16. G. Golovos, G. S. Wilson, J. Moyers, *Anal. Chim. Acta* **64**, 457 (1973).
17. W. R. Matson, R. M. Griffin, G. B. Schreiber, in *Trace Substances in Environmental Health*, D. D. Hemphill, Ed. (Univ. of Missouri Press, Columbia, 1971), pp. 396–406.
18. H. L. Kahn, *J. Chem. Educ.* **43**, A-7 (1966); W. Slavin and S. Slavin, *Appl. Spectrosc.* **23**, 421 (1969).
19. H. L. Kahn, G. E. Peterson, J. E. Schallis, *At. Absorpt. Newsl.* **7**, 35 (1968).
20. M. F. Reed and E. D. Rees, *Am. Lab. (Greens Farms, Conn.)* (Nov. 1970), p. 45; W B. Barnett, *Anal. Chem.* **44**, 695 (1972).
21. H. T. Delves, G. Shepherd, P. Vinter, *Analyst (Lond.)* **96**, 260 (1971); A. E. Moffitt, Jr., P. M. Quinn, L. P. Limtiaco, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1971), p. 8.
22. D. C. Manning and F. Fernandez, *At. Absorpt. Newsl.* **9**, 65 (1970); M. D. Amos, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1970), p. 33; J. P. Matousek, *ibid.* (June 1971), p. 45; J. Y. Hwang, P. A. Ullucci, S. B. Smith, Jr., *ibid.* (Aug. 1971), p. 41; J. W. Robinson and P. L. Slevin, *ibid.* (Aug. 1972), p. 10; M. D. Amos, *ibid.* (Aug. 1972), p. 57.
23. C. J. Pickford and G. Rossi, *Analyst (Lond.)* **97**, 647 (1972); K. G. Brodie and J. P. Matousek, *Anal. Chem.* **43**, 1557 (1971); P. A. Ullucci, C. J. Mokeler, J. Y. Hwang, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1972), p. 63; H. L. Kahn, *ibid.* (Aug. 1971), p. 35; J. P. Matousek and B. J. Stevens, *Clin. Chem.* **17**, 363 (1971).
24. W. R. Hatch and W. L. Ott, *Anal. Chem.* **40**, 2085 (1968).
25. J. Y. Hwang, P. A. Ullucci, C. J. Mokeler, S. B. Smith, Jr., *Am. Lab. (Greens Farms, Conn.)* (Mar. 1973), p. 43.
26. E. N. Pollock and S. J. West, *At. Absorpt. Newsl.* **11**, 104 (1972).
27. O. Menis and T. C. Rains, *Anal. Chem.* **41**, 952 (1969).
28. J. D. Winefordner and T. J. Vickers, *ibid.* **36**, 161 (1964).
29. H. L. Kahn, in *Trace Inorganics in Water*, R. F. Gould, Ed. (Advances in Chemistry Series No. 73, American Chemical Society, Washington, D.C., 1968), pp. 183–229.
30. A. J. Bedrosian, R. K. Skogerboe, G. H. Morrison, *Anal. Chem.* **40**, 854 (1968).
31. W. G. Elliot, *Am. Lab. (Greens Farms, Conn.)*, (Aug. 1971), p. 45.
32. R. S. Braman, L. L. Justen, C. C. Foreback, *Anal. Chem.* **44**, 2195 (1972).
33. A. J. McCormack, S. S. C. Tong, W. D. Cooke, *ibid.* **37**, 1470 (1965).
34. H. Kawaguchi, T. Sakamote, A. Mizuike, *Talanta* **20**, 321 (1973).
35. K. Ohls, K. H. Koch, G. Becker, *Z. Anal. Chem.* **264**, 97 (1973).
36. W. D. Ross, R. E. Sievers, G. Wheeler, Jr., *Anal. Chem.* **37**, 598 (1965); W. D. Ross and R. E. Sievers, in *Developments in Applied Spectroscopy*, E. L. Grove, Ed. (Plenum, New York, 1970), vol. 8, p. 181.
37. E. Bayer, H. P. Muller, R. Sievers, *Anal. Chem.* **43**, 2012 (1971).
38. H. Veening and F. F. K. Huber, *J. Gas Chromatogr.* **6**, 326 (1968); R. E. Sievers, in *Coordination Chemistry*, S. Kirschner, Ed. (Plenum, New York, 1969), p. 270.
39. W. A. Aue and H. H. Hill, Jr., *J. Chromatogr.* **74**, 319 (1972).
40. H. H. Hill, Jr., and W. A. Aue, *ibid.*, p. 311.
41. Y. Shimoishi, *Anal. Chim. Acta* **64**, 465 (1973).
42. K. Ballschmiter, *Z. Anal. Chem.* **254**, 348 (1971).
43. S. D. Rasberry, B. F. Scribner, M. Margoshes, *Appl. Opt.* **6**, 81 (1967); *ibid.*, p. 87.
44. W. J. Treytl, J. B. Orenberg, K. W. Marich, A. J. Saffir, D. Glick, *Anal. Chem.* **44**, 1903 (1972).
45. J. A. Chandler, *Am. Lab. (Greens Farms, Conn.)* (Apr. 1971), p. 50.
46. F. W. Karasek, *Res. Dev.* (Feb. 1970), p. 32.
47. M. Bayard, *Am. Lab. (Greens Farms, Conn.)* (Apr. 1971), p. 15.
48. H. H. Kramer and W. H. Wahl, in *Principles of Nuclear Medicine*, H. N. Wagner, Jr., Ed. (Saunders, Philadelphia, 1968), pp. 811–832.
49. J. N. Weaver, *Am. Lab. (Greens Farms, Conn.)* (Mar. 1973), p. 36.
50. A. R. Byrne and D. Gorene, *Anal. Chim. Acta* **59**, 81 (1972); A. R. Byrne, *ibid.*, p. 91; K. Samsahl, *Sci. Total Environ.* **1**, 65 (1972).
51. J. R. Rottschafer, *Talanta* **19**, 163 (1972).
52. S. K. Bhagat, W. H. Funk, R. H. Filby, K. R. Shah, *J. Water Pollut. Control Fed.* **43**, 2414 (1971); M. A. Kay, D. M. McKown, D. M. Gray, J. R. Eichor, G. T. Vogt, *Am. Lab. (Greens Farms, Conn.)* (July 1973), p. 39; V. P. Guinn, *J. Am. Oil Chem. Soc.* **45**, 767 (1968).
53. J. G. Osteryoung and R. A. Osteryoung, *Am. Lab. (Greens Farms, Conn.)* (July 1972), p. 8.
54. R. E. Frazier, *J. Am. Waterworks Assoc.* **64**, 391 (1972).
55. J. H. Christie, J. Osteryoung, R. A. Osteryoung, *Anal. Chem.* **45**, 210 (1973).
56. E. B. Owens, *Appl. Spectrosc.* **21**, 1 (1967); ——— and N. A. Giardine, *Anal. Chem.* **35**, 1172 (1963); C. A. Evans, Jr., and G. H. Morrison, *ibid.* **40**, 869 (1968); A. J. Ahearn, Ed., *Trace Analysis by Mass Spectrometry* (Academic Press, New York, 1972).
57. R. A. Bingham and R. M. Elliott, *Anal. Chem.* **43**, 43 (1971).
58. R. Brown, P. Powers, W. A. Wolstenholme, *ibid.*, p. 1079.
59. J. P. Yurachek, G. G. Clemena, W. W. Harrison, *ibid.* **41**, 1667 (1969); W. W. Harrison, G. G. Clemena, C. W. Magee, *J. Assoc. Offic. Anal. Chem.* **54**, 929 (1971); R. Brown, M. L. Jacobs, H. E. Taylor, *Am. Lab. (Greens Farms, Conn.)* (Nov. 1972), p. 29; I. H. Crocker and W. F. Merritt, *Water Res.* **6**, 285 (1972).
60. J. R. Rhodes, *Am. Lab. (Greens Farms, Conn.)* (July 1973), p. 57; J. P. Hurley, V. L. DaGragnano, J. M. Mathiesen, *Res. Dev.* (Dec. 1970), p. 14; W. G. Wood, *Am. Lab. (Greens Farms, Conn.)* (Feb. 1972), p. 27; R. Woldseth, D. E. Porter, R. S. Frankel, *Ind. Res.* (Feb. 1971), p. 46.

61. J. R. Rhodes, A. H. Pradzynski, C. B. Hunter, J. S. Payne, J. L. Lindgren, *Environ. Sci. Technol.* **6**, 922 (1972).
62. U. M. Cowgill, in *Developments in Applied Spectroscopy*, L. R. Pearson and E. L. Grove, Eds. (Plenum, New York, 1966), vol. 5, pp. 3–23.
63. R. A. Long, *Am. Ind. Hyg. Ass. J.* **33**, 343 (May 1972).
64. R. Frankel and R. Woldseth, *Res. Dev.* (June 1973), p. 38.
65. T. B. Johansson, R. Akselsson, S. A. E. Johansson, *Nucl. Instrum. Methods* **84**, 141 (1970).
66. J. J. Kraushaar, R. A. Ristinen, H. Rudolph, W. R. Smythe, *Bull. Am. Phys. Soc.* **16**, 545 (1971); H. Rudolph, R. Ristinen, W. Smythe, A. Alfrey, S. Contiguglia, *ibid.* **17**, 548 (1972).
67. G. M. George, L. J. Frahm, J. P. McDonnell, *J. Assoc. Offic. Anal. Chem.* **56**, 793 (1973).
68. D. J. Myers and J. Osteryoung, *Anal. Chem.* **45**, 267 (1973).
69. T. R. Gilbert and D. N. Hume, *Anal. Chim. Acta* **65**, 451 (1973).
70. E. N. Pollock and S. J. West, *At. Absorpt. Newsl.* **11**, 104 (1972).
71. T. Maruta, T. Takeuchi, M. Suzuki, *Anal. Chim. Acta* **58**, 452 (1972).
72. G. Sighinolfi, *At. Absorpt. Newsl.* **11**, 96 (1972).
73. J. K. Foreman, T. A. Gough, E. A. Walker, *Analyst (Lond.)* **95**, 797 (1970).
74. F. E. Butler, *Am. Ind. Hyg. Assoc. J.* **30**, 559 (1969).
75. D. L. Bokowski, *ibid.* **29**, 474 (1968).
76. W. D. Ross and R. E. Sievers, *Environ. Sci. Technol.* **6**, 155 (1972).
77. D. J. Eisentraut, D. J. Griest, R. E. Sievers, *Anal. Chem.* **43**, 2003 (1971).
78. W. R. Wolf, M. L. Taylor, B. M. Hughes, R. O. Tiernan, R. E. Sievers, *ibid.* **44**, 616 (1972).
79. G. Kaiser, E. Grallath, P. Tschopel, G. Tölg, *Z. Anal. Chem.* **259**, 257 (1972).
80. R. J. Gajan, J. H. Gould, J. O. Watts, J. A. Fiorino, *J. Assoc. Offic. Anal. Chem.* **56**, 876 (1973).
81. J. Lener and B. Bibr, *J. Agric. Food Chem.* **19**, 1011 (1971).
82. Y. Takagi and M. Satake, *J. Chem. Soc. Jap.* **11**, 2207 (1972).
83. C. R. Parker, J. Rowe, D. P. Sandoz, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1973), p. 53.
84. R. R. Ross, J. G. Gonzalez, D. A. Segar, *Anal. Chim. Acta* **63**, 205 (1973).
85. W. F. Davidson and W. L. Secrest, *Anal. Chem.* **44**, 1080 (1972).
86. K. H. Schaller, H. G. Essing, H. Valentin, G. Schaecke, *Z. Klin. Chem. Klin. Biochem.* **10**, 434 (1972).
87. E. E. Cary and W. H. Allaway, *J. Agric. Food Chem.* **19**, 1159 (1971).
88. K. M. Hambidge, *Anal. Chem.* **43**, 103 (1971).
89. J. Savory, P. Mushak, F. W. Sunderman, Jr., *J. Chromatogr. Sci.* **7**, 674 (1969).
90. G. H. Booth, Jr., and W. J. Darby, *Anal. Chem.* **43**, 831 (1971).
91. L. C. Hansen, W. G. Scribner, R. W. Gilbert, R. E. Sievers, *ibid.*, p. 349.
92. O. Johansen and E. Steinnes, *Acta Agric. Scand.* **22**, 103 (1972).
93. J. Jago, P. E. Wilson, B. M. Lee, *Analyst (Lond.)* **96**, 349 (1971).
94. A. L. Gelman, *J. Sci. Food Agric.* **23**, 299 (1972).
95. C. W. Fuller, *Anal. Chim. Acta* **62**, 442 (1972).
96. M. R. Roschnik, *Mitt. Geb. Lebensmittelunters. Hyg.* **63**, 206 (1972).
97. W. B. Barnett and H. L. Kahn, *Clin. Chem.* **18**, 923 (1972).
98. M. Glenn, J. Savory, L. Hart, T. Glenn, J. Winefordner, *Anal. Chim. Acta* **57**, 263 (1971).
99. B. J. Stevens, *Clin. Chem.* **18**, 1379 (1972).
100. D. H. Strunk and A. A. Andreason, *At. Absorpt. Newsl.* **6**, 111 (1967).
101. H. Spector, S. Glusman, P. Jatlow, D. Seligson, *Clin. Chim. Acta* **31**, 5 (1971).
102. K. L. Cheng and R. H. Bray, *Anal. Chem.* **25**, 655 (1953).
103. M. P. Bratzel, Jr., *ibid.* **44**, 372 (1972).
104. M. Harth, D. Haines, D. C. Bondy, *Am. J. Clin. Pathol.* **59**, 423 (1973).
105. M. A. Hildon and G. R. Sully, *Anal. Chim. Acta* **54**, 245 (1970).
106. K. I. Aspila, C. L. Chakrabarti, M. P. Bratzel, Jr., *Anal. Chem.* **44**, 1718 (1972).
107. E. Norval and L. R. P. Butler, *Anal. Chim. Acta* **58**, 47 (1972).
108. R. Woodriff and J. F. Lech, *Anal. Chem.* **44**, 1323 (1972).
109. J. Y. Hwang, P. A. Ullucci, S. B. Smith, Jr., A. L. Malenfant, *ibid.* **43**, 1319 (1971).
110. G. K. Pagenkopf, D. R. Newman, R. Woodriff, *ibid.* **44**, 2248 (1972).
111. J. F. Rosen and E. E. Trinidad, *J. Lab. Clin. Med.* **80**, 567 (1972).
112. N. P Kubasik, M. T. Volosin, M. H. Murray, *Clin. Biochem.* **5**, 266 (1972).
113. ———, *Clin. Chem.* **18**, 410 (1972).
114. R. J. Segal, *ibid.* **15**, 1124 (1969).
115. W. Oelschlager and E. Schwarz, *Z. Anal. Chem.* **258**, 203 (1972).
116. K. Boloder, N. Ivicic, B. Svigir, *Mikrochim. Acta* **1971**, 341 (1971).
117. R. J. Gajan and D. Larry, *J. Assoc. Offic. Anal. Chem.* **55**, 727 (1972).
118. ———, *ibid.*, p. 733.
119. K. Fletcher, *J. Sci. Food Agric.* **22**, 260 (1971).
120. L. J. Purdue, R. E. Enrione, R. J. Thompson, B. A. Confield, *Anal. Chem.* **45**, 527 (1973).
121. D. G. Mitchell, F. J. Ryan, K. M. Aldous, *At. Absorpt. Newsl.* **11**, 120 (1972).
122. H. Lyons and F. E. Quinn, *Clin. Chem.* **17**, 152 (1971).
123. P. P. Donovan and D. T. Feeley, *Analyst (Lond.)* **94**, 879 (1969).
124. D. C. Hilderbrand, S. R. Koirtyohann, E. E. Pickett, *Biochem. Med.* **3**, 437 (1970).
125. E. D. Olsen and P. I. Jatlow, *Clin. Chem.* **18**, 1312 (1972).
126. M. M. Joselow and J. D. Bogden, *At. Absorpt. Newsl.* **11**, 99 (1972).
127. H. T. Delves, *Analyst (Lond.)* **95**, 431 (1970).
128. D. C. Manning, *Am. Lab. (Greens Farms, Conn.)* (Aug. 1973), p. 37.
129. A. A. Cernik and M. H. P. Sayers, *Br. J. Ind. Med.* **28**, 392 (1971).
130. M. P. Bratzel, Jr., and C. L. Chakrabarti, *Anal. Chim. Acta* **61**, 25 (1972).
131. S. H. Omang, *ibid.* **55**, 439 (1971).
132. B. Searle, W. Chan, B. Davidow, *Clin. Chem.* **19**, 76 (1973).
133. J. L. Hansen, *Am. J. Med. Technol.* **34**, 1 (1968).
134. F. Bek, J. Janouskova, B. Moldan, *Chem. Listy* **66**, 867 (1972).
135. R. K. Munns and D. C. Holland, *J. Assoc. Offic. Anal. Chem.* **54**, 202 (1971).
136. W. R. Hatch and W. L. Ott, *Anal. Chem.* **40**, 2085 (1968)
137. G. Lindstedt, *Analyst (Lond.)* **95**, 264 (1970).
138. J. Y. Hwang and P. A. Ullucci, *Am. Lab. (Greens Farms, Conn.)* (Dec. 1970), p. 50.
139. J. D. Brooks and W. E. Wolfram, *ibid.* (Dec. 1971), p. 54.
140. D. H. Klein, *J. Chem. Educ.* **49**, 7 (1972).
141. J. F. Kopp, M. C. Longbottom, L. B. Lobring, *J. Am. Water Works Assoc.* **64**, 20 (1972).
142. R. H. Filby, A. I. Davis, K. R. Shah, W. A. Haller, *Mikrochim. Acta* **1970**, 1130 (1970).
143. K. K. Pillay, C. C. Thomas, Jr., J. A. Sondel, C. M. Hyche, *Anal. Chem.* **43**, 1419 (1971).
144. A. R. Byrne, M. Kermelj, L. Kosta, *J. Radioanal. Chem.* **6**, 325 (1970).
145. M. W. Heitzman and R. E. Simpson, *J. Assoc. Offic. Anal. Chem.* **55**, 960 (1972).
146. H. L. Rook, T. E. Gills, P. D. LaFleur, *Anal. Chem.* **44**, 1114 (1972).
147. D. H. Anderson, J. H. Evans, J. J. Murphy, W. W. White, *ibid.* **43**, 1511 (1971).
148. M. Hinkle and R. E. Learned, *U.S. Geol. Surv. Prof. Pap. 650-D* (1969), p. D251.
149. A. E. Moffitt, Jr., and R. E. Kupel, *Am. Ind. Hyg. Assoc. J.* **32**, 614 (1971).
150. W. A. Klemm and N. R. Fetter, *At. Absorpt. Newsl.* **11**, 108 (1972).
151. W. A. Willford, R. J. Hesselberg, H. L. Bergman, *J. Assoc. Offic. Anal. Chem.* **56**, 1008 (1973).
152. G. Westöö, *Acta Chem. Scand.* **21**, 1790 (1967).
153. ———, *ibid.* **22**, 2277 (1968).
154. ———, *ibid.* **20**, 2131 (1966).
155. W. H. Newsome, *J. Agric. Food Chem.* **19**, 567 (1971).
156. C. A. Bache and D. J. Lisk, *Anal. Chem.* **43**, 950 (1971).
157. L. Magos, *Analyst (Lond.)* **96**, 847 (1971).
158. J. C. Gage and J. M. Warren, *Ann. Occup. Hyg.* **13**, 115 (1970).
159. G. L. Baughman, M. H. Carter, N. L. Wolf, R. G. Zepp, *J. Chromatogr.* **76**, 471 (1973).
160. B. Johansson, R. Ryhage, G. Westöö, *Acta Chem. Scand.* **24**, 2349 (1970).
161. L. Magos and T. W. Clarkson, *J. Assoc. Offic. Anal. Chem.* **55**, 966 (1972).
162. L. R. Kamps and B. McMahon, *ibid.*, p. 590.
163. V. Zelenko and L. Kosta, *Talanta* **20**, 115 (1973).
164. E. R. Purvis and N. K. Peterson, *N.J. Agric. Exp. Stn. Rutgers Univ. J. Ser.* (1955), pp. 223–228.
165. R. A. A. Muzzarelli and R. Rocchetti, *Anal. Chim. Acta* **64**, 371 (1973).
166. R. S. Barratt, R. Belcher, W. I. Stephen, P. C. Uden, *ibid.* **59**, 59 (1972).
167. R. B. Baird, S. Pourian, S. M. Gabrielian, *Anal. Chem.* **44**, 1887 (1972).
168. "Perkin-Elmer High-Sensitivity Arsenic/Selenium Sampling System" (Perkin-Elmer Corporation Bulletin PEP 117110, Norwalk, Conn., 1972).
169. W. H. Allaway and E. E. Cary, *Anal. Chem.* **36**, 1359 (1964).
170. J. H. Watkinson, *ibid.* **38**, 92 (1966).
171. H. K. J. Hahn, R. V. Williams, R. E. Burch, J. F. Sullivan, E. A. Novak, *J. Lab. Clin. Med.* **80**, 718 (1972).
172. R. Woodriff, B. R. Culver, D. Shrader, A. B. Super, *Anal. Chem.* **45**, 230 (1973).
173. M. P. Bratzel, Jr., C. L. Chakrabarti, R. E. Sturgeon, M. W. McIntyre, H. Agemian, *ibid.* **44**, 372 (1972).
174. A. Engberg, *Analyst (Lond.)* **98**, 137 (1973).
175. J. M. Bowen, *ibid.* **97**, 1003 (1972).
176. J. D. Smith, *Anal. Chim. Acta* **57**, 371 (1971).
177. G. M. Shkolnik and R. F. Bevill, *At. Absorpt. Newsl.* **12**, 112 (1973).
178. R. Rioni, F. Innocenti, R. Mazzuoli, *ibid.* **11**, 102 (1972).
179. R. M. Welch and W. H. Allaway, *Anal. Chem.* **44**, 1644 (1972).
180. D. E. Robertson and R. Carpenter, "1972 Report Issue of Battelle Pacific Northwest Laboratory" (Battelle Pacific Northwest Laboratory, Richland, Wash., 1972), p. 71.
181. D. Clark, R. M. Dagnall, T. S. West, *Anal. Chim. Acta* **63**, 11 (1973).
182. V. B. Grossman and A. S. Inglis, *Anal. Chem.* **43**, 1903 (1971).