A CENTURY OF ANALYTICAL EXCELLENCE

Pesticides, Their Analysis and the AOAC: An Overview of a Century of Progress (1884–1984)

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The Early Years (1884–1942)

In this centennial year of the founding of AOAC, it is almost impossible for us to comprehend just what it was like to live in the year 1884. Therefore, the reader is asked to digress briefly to reflect on events and conditions in the United States at the time our Association was founded. Such reflections will emphasize the incredible growth of science and technology as well as the rapid development of the American nation and world civilization.

Visualize the year 1884: The population of the United States was about 55 million and the national debt stood at the staggering figure of 2 billion dollars. Grover Cleveland had just been elected to succeed Chester A. Arthur in the White House, and there were 38 stars in our flag. There was talk about opening up the Oklahoma Territory to settlement, but this would not occur for 5 more years. The Industrial Revolution had gained full momentum, and a modern engineering marvel, the Brooklyn Bridge, was opened last year. Only 5 years had passed since Alexander Graham Bell had carried on the first telephone conversation, and 13 more years would pass before Marconi could successfully send short-distance radio messages. Although railroads were fully operational, automobiles were still in the experimental stage (Daimler; Benz). Some recent inventions were barbed wire (Glidden), the phonograph and incandescent lamp (Edison), electric fan (Wheeler), electric flat iron (Seeley), steam turbine (Parsons), and the fountain pen (Waterman) (1). These developments are mentioned to emphasize the fact that the technology and apparatus required for modern pesticide research were just beginning to emerge; only a very small percentage of the devices currently used in research existed in the year 1884. Broad advances in the areas of chemistry, physics, medicine, communications and information, engineering, and transportation slowly and steadily provided the building blocks for our present capabilities. Also, during the past several decades we have seen that requirements for national defense, space exploration, competition among nations for world markets, and public demand for an improved quality of life and a safe environment have accelerated the advancement of science.

In 1884, pesticide formulations were concoctions containing one or more of the following ingredients: tobacco, soap, turpentine, various oils, kerosene, sulfur, lime, phosphorus, mercuric chloride, arsenic, hydrocyanic acid, phenol, cresol, pyrethrum, and naphthalene (2). Paris green, an aceto-meta-arsenite of copper [$Cu(CH_3COO)_2{\cdot}3Cu(AsO_2)_2$], had come into common usage as an insecticide. Bordeaux mixture, a combination of lime and copper sulfate, was discovered to have fungicidal properties by Millardet in France in 1883. Bordeaux mixture and Paris green could be safely combined to produce a spray with both insecticidal and fungicidal properties. London purple, a mixture of calcium arsenate, calcium arsenite, and other products including a small amount of dye, was recommended as a substitute for Paris green. The name "London purple" was given to the material because it was originally an arsenical by-product of the magenta dye industry in London (2). Oddly enough, DDT had been synthesized by Zeidler in Germany in 1874 but its insecticidal properties would not be discovered until 1939. This list of pesticides appears completely inadequate when compared with the many products available to us today. However, if we begin with the earliest records of pesticides found on stone tablets which described the use of red squill (dried bulbs of the lily family) as a rat poison, include Homer's description of the use of sulfur for fumigation and other forms of pest control in about 1000 BC, and all other discoveries up to the use of turpentine to repel and kill insects in 1787 (2), it becomes obvious that more progress was made during the nineteenth century than in all previously recorded history. In the year 1984, even a cursory view of the history of pesticides shows that the knowledge, development, and usage of these substances are increasing exponentially with time.

Conditions which led to the organization of the Association of Official Agricultural Chemists (AOAC) centered around the new chemical fertilizer industry which had begun to fluorish late in the nineteenth century. Several states passed legislation which required that the N-P-K content be placed in each bag. Consequently, chemists from government and industry made three separate attempts in 1880 and 1881 to coordinate their work; however, all failed because of disputes over the choice of methods. In 1884, J. T. Henderson, Commissioner of Agriculture, State of Georgia, called a conference in Atlanta to organize an association to adopt uniform analytical procedures. This group wrote a constitution which allowed only regulatory chemists to vote on the adoption of methods; however, others could participate in discussions and investigations. The fertilizer industry subsequently recognized the urgent need for uniform methods and recommended that the constitution be adopted (3). Thus, AOAC was born later that same year at Philadelphia. From this simple beginning, AOAC (known as the Association of Official Analytical Chemists since 1965) has grown to encompass the development and adoption of uniform methods for virtually every field of the analytical sciences pertaining to agriculture, public health and safety, consumer protection, and quality of the environment. The Association has quickly outgrown its present name and is no longer just an organization for chemists but is truly an Association of all analytical scientists.

Prior to writing this article, the author searched the archives of AOAC at Arlington, VA, and found that the early activities of the Association were published as proceedings by the U. S. Department of Agriculture. Although nothing pertaining to the analysis of pesticides could be found before 1899, some of the entomology reports were quite interesting and should be briefly shared with the reader. An extensive report was presented in 1886 concerning the production and use of the insect powder "Buhach" (4). The product was produced at Stockton, CA, from dried flowers of *Pyrethrum cinerariafolium* grown on 300 acres in Merced County, CA, and sold wholesale for 45 to 50 cents a pound. The application of the

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material as a powder, tea, or tincture was vividly described along with its insecticidal effects. Several testimonials were presented concerning its low mammalian toxicity as follows: 1) "Workmen in the manufacturing plant continuously breathed the fine dust for several hours at a time and never suffered adverse effects," 2) "One teaspoonful of the alcoholic extract of Buhach was administered to a certain person afflicted with tape-worm; the dose was repeated each hour for ten consecutive hours, with the effect of removing the tape-worm without in the least degree injuring the patient." 3) At the stable of the Buhach plantation several tons of the dried stems were fed to the horses; "the latter appeared to relish it very much" and no injury could be discovered. Although these testimonials were useful in 1886 and contained many basic elements of modern toxicology, they would hardly be admissable by regulatory agencies as good laboratory practice experiments in 1984.

In entomology reports of 1886 (5), the blister beetle (*Cantharis nuttalli* Say) was reported to cause great damage to bean crops in North Dakota; the remedy was to drive them into windrows of straw which were then burned. In another report, the wooly aphis (*Schizoneura lanigera*) was causing extensive damage to apple trees in California; the remedy was to spray with a mixture containing one-half pound of tobacco and one-half pound of whale oil soap per gallon of water. The mixture was to be applied at about 130°F and the process repeated in about one week. A comparison of these remedies with current practices will emphasize the progress that has been made in pest control during the past century.

At the 15th Annual Convention of the AOAC in 1898, the president of the Association recognized that the value of products such as tobacco powder and extracts, which were coming into extensive use, was chiefly dependent on the nicotine content and called for methods to determine this ingredient. Furthermore, methods for arsenical powders and fungicides were also needed; therefore, he called for the appointment of a referee to investigate methods for the valuable ingredients in these products (6). Thus, the following year (1899), the first AOAC report on fungicides and insecticides was presented to the convention by Referee L. A. Voorhees. This report included methods for determining nicotine, arsenic, cyanogen, copper, and formaldehyde which specified volumetric or gravimetric techniques after various chemical reactions and manipulations (7). With this modest beginning, a continuous effort has been sustained by AOAC to obtain, develop, validate, and adopt analytical procedures for pesticides that are legally and mutually acceptable to both government and industry. These methods were initially published annually in the *Proceedings of the Annual Meeting of the AOAC* and subsequently in the *Journal of the AOAC*, which succeeded it in 1915 and has appeared continuously since its inception. The *Journal* began accepting contributed articles in 1923, and since 1920, AOAC has also published *Official Methods of Analysis* every 5 years. Through the years, these publications have been invaluable as references to accepted procedures for pesticide analysis; the *Journal* has also provided for the rapid publication of new methods not yet subjected to the rigorous evaluation required for official adoption.

From the turn of the century until the beginning of the synthetic organic pesticide era in 1942, many new products and ideas were advanced for pest control. Various new compounds of arsenic came into use and new fumigants included *p*-dichlorobenzene, ethylene oxide, ethylene dichloride, and methyl bromide. Geraniol was found to attract the Japanese beetle, and alkyl phthalates to repel insects. Cubé was being tested as an insecticide, and sesame oil was discovered to synergize pyrethrum. The airplane was first used at Troy, OH, to distribute insecticides in 1921. The age of synthetic organic pesticides was beginning to dawn with the commercial production of pentachlorophenol in 1936 and the discovery of hexachlorobenzene in 1941 (2). The development of new analytical chemical techniques during this period proceeded at a snail's pace; only the electrolytic determination of copper was added to the conventional volumetric and gravimetric methods for pesticide analysis.

On the regulatory scene, an arsenic poisoning incident involving some 6000 persons in England who had consumed contaminated beer resulted in about 70 deaths. This prompted the British to establish a tolerance of 0.01 gr (grains) As_2O_3/lb of solid food (1 ppm = 0.007 gr/lb) in 1903. A Federal Pure Food and Drug Act was passed in 1906; however, proof that an adulterated food was a potential health hazard was required prior to corrective action. The Federal Insecticide Act was passed in 1910, and in 1927, the Food and Drug Administration established a tolerance of 0.025 gr As_2O_3/lb for fruits and vegetables in interstate commerce. Later, in 1923, accurate methods for low levels of lead became available and a tolerance of 0.025 gr Pb/lb of commodity was also set because of the widespread use of lead arsenate. The Food, Drug and Cosmetic Act of 1938 provided more extensive protection to the consumer than the previous act of 1906, because provision was made to establish safe tolerances for deleterious substances added to foods (2).

It should be pointed out that Harvey W. Wiley was a key figure in the founding and development of AOAC. Dr. Wiley, supported by the official methods of AOAC, was primarily responsible for the passage of the Pure Food and Drug Act of 1906. As the first administrator of this Act, he came under severe pressure from industry; however, even after his retirement from the Department of Agriculture in 1912, he continued to speak out for consumer protection until his death in 1930 (3).

As we entered World War II and the era of synthetic organic pesticides, most of the analytical chemical procedures were still confined to the analysis of formulations except for the As and Pb residue determinations previously mentioned. Analytical technology required for trace-level analyses was simply not available to keep pace with our knowledge of chemistry and the development of pesticides.

The Era of Synthetic Organic Pesticides (1942–Present)

DDT is probably the most widely known, used, and abused pesticide in all recorded history. Although first synthesized in 1874, it was not tested as an insecticide until 1939. A small amount of the compound was brought into the United States in 1942 and tests soon revealed its outstanding insecticidal properties. The author has selected this event as the beginning of the era of synthetic organic pesticides. Production was begun almost immediately and essentially the entire output was used by the armed forces to control body lice, mosquitoes, and other pests during World War II. Large quantities of the pesticide were produced for post-war use, and soon an entire family of synthetic organochlorine compounds was in widespread use. In addition to DDT, this class of chemicals included chlordane, toxaphene, lindane, methoxychlor, aldrin, dieldrin, heptachlor, and others. Residues of many of these compounds were highly persistent in the environment. Then in about 1946, synthetic organophosphorus insecticides such as parathion and TEPP, produced by German research, were also introduced into the United States.

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Many compounds of this general class also quickly came into general use. These chemicals differed from organochlorine compounds in that they were generally more toxic to warm-blooded animals and less persistent in the environment. In the 1950s, another class of synthetic insecticides known as carbamates came into use, and a large family of these compounds soon developed.

Concurrent with the development of organochlorine, organophosphorus, and carbamate insecticides, many classes of herbicides were also being produced. These included chlorinated phenoxy acids, *S*-triazines, phenylureas, carbamates, phenols, dinitroanilines, chlorinated benzoic acids, and others. During this same period of about two decades, many other compounds of pesticidal activity came into use as rodenticides, repellants, attractants, sexual sterilants, fungicides, nematocides, acaricides, bactericides, miticides, synergists, defoliants, fumigants, growth regulators, algicides, mulloscicides, etc. All of these chemicals, when added to those already in use prior to 1942, constitute a plethora of compounds available for pesticidal evaluation and use. Hence, there was an exponential increase in the demand for analytical chemical procedures which were both specific and sensitive for determining residues of these individual chemicals and their admixtures.

As we entered the era of synthetic organic pesticides in 1942, the development of analytical chemical technology had not kept pace with the requirements for it. Furthermore, with the addition of several hundred new pesticides of many classes during the 1940s and 1950s, problems facing analytical scientists seemed almost insurmountable, particularly in the area of residue analysis for regulatory purposes.

Instrumentation for infrared, visible, and ultraviolet absorption spectrometry became generally available during the 1940s and was very useful for the analysis of pesticide formulations. Polarography was also used in limited applications. However, these methods were not easily adapted to the analysis of residues in food, feed, and environmental samples. The most widely used residue methods of this period were based on the formation of a colored product followed by a spectrophotometric measurement of its intensity in the visible portion of the spectrum. Examples of these are the classical Schechter-Haller method for DDT (8) and the Averell-Norris method for parathion (9). Another useful procedure developed during this period, which remains equally useful today, is the enzymatic method based on chlolinesterase inhibition (10). This method, which may now be quantified by change in pH, colorimetrically or manometrically, is useful for the determination of organophosphorus insecticides and to measure the extent of any exposure of humans or animals to such compounds.

Most analyses for residues of pesticides consist of a three-step process involving, 1) the extraction of residues from the substrate, 2) separation of the residues from coextractives (known as cleanup), and 3) measurement of the extracted residues. Considerable progress was made in all three of these steps during the 1940s and 1950s; however, experiments with rudiments of chromatography primarily for use in the cleanup step would prove to be the key to successful analyses of residues in the future. Tswett (11), whose name in Russian means color (12), is usually credited with the process known as chromatography. His experiments, reported in 1906, dealt with the separation of solutions of colored plant pigments by percolating them through columns of solid adsorbents. The colored plant pigments were separated into distinct colored bands by a kind of liquid-solid or liquid-adsorption chromatography. Whether Tswett's coining of the term chromatography (color writing) alluded to the colored bands on the column or to his own writings is not known.

As early as 1512, Brunschwig (13) had described a primative form of gas chromatography for purifying ethyl alcohol (14, 15). Also, in this very brief review of chromatography, the author is compelled to cite instructions on this subject given by the *Supreme Scientist of the Universe*, in about 1491 BC; "So Moses brought Israel from the Red Sea, and they went out into the wilderness of Shur; and they went three days in the wilderness, and found no water. And when they came to Marah, they could not drink of the waters of Marah, for they were bitter; therefore the name of it was called Marah. And the people murmured against Moses, saying 'What shall we drink'? And he cried unto the Lord; and the Lord shewed him a tree, which when he had cast into the waters, the waters were made sweet: there he made for them a statute and an ordinance, and there he proved them" (16).

Regardless of where the reader chooses to put the origin of the chromatographic process, it is clear that the concept, as applied to analytical chemistry, was dormant until the mid-1940s when adsorption columns came into use for separating pesticide residues from coextractives which interfered with the analysis. Liquid-liquid chromatography, described in 1941 (17), was later developed into paper chromatography (18). An early application of paper chromatography to pesticide analysis was that of Metcalf and March (19) for parathion and related phosphate esters. Although Martin and Synge (18) had presented the basic principles of gas chromatography (GC) in their 1948 paper, little was done to develop the procedure before the work of James and Martin (20) in 1952. GC then developed very rapidly and became one of the outstanding methods for analysis. Its usefulness for the analysis of pesticides was limited to formulations because the detectors were not specific; however, a combustion furnace, titration cell, and coulometer were soon placed in tandem with the gas chromatograph for the analysis of pesticides which contained chlorine or sulfur (21).

In brief summary of the events during the 20-year period leading into the 1960s, hundreds of synthetic organic pesticides of many chemical classes became available for use; sensitive and specific methods were required for their analysis, particularly from the residue aspect. Infrared, visible, and ultraviolet spectrometry became common, and many colorimetric methods were developed. Outstanding progress was made in the area of separation science with the development of liquid-solid column chromatography, paper chromatography, and gas-liquid chromatography. Sensitivity for analyzing residues was brought from the milligram to the microgram level. A popular guide to the analysis of such residues during that period was the classical textbook of Gunther and Blinn (22). In reviewing the archives for this period at AOAC, the author found that the names of the Associate Referees would literally constitute a Who's Who in pesticide analysis. AOAC had indeed been hard at work, and many procedures based on new technology had appeared in the *Official Methods of Analysis* of the AOAC by 1960. It was also noted that the old section heading "Insecticides and Fungicides" was replaced by "Economic Poisons" in 1950. However, this term was short-lived and, in 1955, under the editorship of William Horwitz, the present category "Pesticides" was adopted. The *Journal* of the AOAC and meetings and workshops of the Association continued to provide forums for the development of analytical procedures for pesticides.

By the mid 1960s, several events had occurred which would change the future of pesticide analysis. First, a highly sensi-

tive detector based on the ability of certain functional groups, such as halogens, nitro groups, peroxides, and others, to capture low energy electrons was reported by Lovelock and Lipsky (23). The detector was almost immediately coupled with a gas chromatograph and used for the analysis of chlorinated pesticides (24, 25). This system, known as electron capture gas chromatography (EC-GC), was shown to increase the sensitivity for analyzing halogenated pesticides by a factor of 10,000, making the detection of picogram amounts possible. Second, Rachel L. Carson, an American biologist and science writer, published her book *Silent Spring* in 1962, which aroused public and government concern about the adverse effects of environmental pollutants. Susequently, large sums of public funds were made available for research, monitoring, and regulation of such materials which included pesticides. These two events more than any others set the scene for extensive work in the area of pesticide analysis.

In the 1950s, thin layer chromatography (TLC), which combines desirable features of liquid-solid column chromatography with paper chromatography, was introduced as an analytical procedure. At first, the method was considered only qualitative or semiquantitative at best. However, pioneering work by Beroza et al. (26) and others has brought the technique to acceptable levels of accuracy and precision for quantitative analysis. The method is also well suited for confirmatory tests. Also, beginning in 1965, Bowman and Beroza published a series of papers which described the usefulness of partition values (p-values) in selecting solvents for pesticide extraction, cleanup, and confirmation of identity of the residues (27–29). The EC-GC system previously described for halogenated pesticides responded poorly to the general class of organophosphorus pesticides which were widely used. This gap in methodology was bridged by the development of the alkali flame ionization detector (AFID) of Giuffrida (30) and the flame photometric detector (FPD) of Brody and Chaney (31), which was sensitive and specific for phosphorus or sulfur. The FPD was extensively evaluated for gas chromatographic analysis of phosphorus and sulfur-containing pesticides by Bowman and Beroza, and in 1968, they reported an improvement of the detector which simultaneously presented phosphorus- and sulfur-specific chromatograms on separate channels and also provided for an estimation of the molecular P and S content of the gas chromatographic peak (32). Thousands of publications based on gas chromatographic analysis of pesticide residues appeared in the scientific literature during the ensuing decade. Many of the compounds not directly amenable to gas chromatography were derivatized or otherwise modified prior to analysis.

One of the major deficiencies in gas chromatographic methodology for pesticides had been the absence of detectors sensitive and specific for nitrogen-containing compounds. Coulson (33) addressed this need by placing an electrolytic conductivity cell in tandem with a reduction furnace (nickel catalyst; hydrogen carrier gas) which converted the N-compounds to ammonia. This system was evaluated by Patchett (34) and others and further developed by Hall (35). Although sensitivities to 0.1 ng organic nitrogen with about a 10,000:1 selectivity have been reported (34), operation of the system in the N-mode has not been as popular as the Cl-mode. Another detector useful for the analysis of N-containing compounds is the "rubidium-sensitized" system which responds to both N- and P- containing compounds. After experimental use for several years, the detector became sufficiently reliable for routine use after the rubidium salt was placed into an electrically heated bead and the low hydrogen flow (1–3 mL/min) was precisely controlled (36). Both the electrolytic conductivity and rubidium-sensitized detectors are useful for the analysis of residual N-containing pesticides such as carbamates; however, the instability of many of these compounds may require derivatization or an alternative means of analysis.

A comprehensive series of reviews of the state-of-the-art of pesticide analysis was edited by Bowman in 1975 (37–39). Experts in the field dealt with the analytical chemistry of the various classes of chemicals, types of methods, sampling, and alternative means to achieve the desired biological control. In writing on the subject of carbamate analysis, which remains one of the most difficult classes, H. W. Dorough said, "One of the most disturbing aspects of carbamate residues analysis involves what might be referred to as laboratory-specific methods." Dorough went on to explain that while the laboratory which developed the method continued to report good results, others simply could not make it work. This phenomenon was attributed primarily to the omission of a vital point in the residue procedure which, on the surface, might appear insignificant (40). Most analytical chemists have encountered this problem many times, and its continued presence emphasizes the need for wide participation in the interlaboratory activities of AOAC. Because of the extensive collaborative tests among laboratories which are required for the adoption of a procedure, there are no "laboratory-specific" official methods of AOAC. The adoption of official methods does take time and, of necessity, lags the state-of-the-art; however, this period can be held to a minimum by wide laboratory participation in the process.

In this same series of reviews (37–39), the editor emphasized two problems that still require our attention (41). First, residues of pesticides in environmental samples cannot be analyzed by present methods unless they are extracted from the substrate, and the concern for efficient extraction of such residues has not been commensurate with its importance. Through the years, extraction techniques have progressed from "surface stripping" with nonpolar solvents, through blending with solvents of medium polarity, to exhaustive procedures using more polar mixtures via reflux or Soxhlet extraction. Recoveries of biologically incorporated or weathered residues have increased as techniques improved. However, results from tests with radiolabeled pesticides have revealed that significant amounts of the residual radioactivity remained unextracted even with use of the most rigorous techniques (42, 43). Every effort should be made to develop and use efficient extraction procedures; the nature and toxicological significance of the bound residues should also be determined. Second, tentative identification of pesticide residues in samples of unknown treatment history is often made on the basis of one determinative procedure. It is imperative that such identifications be confirmed (or rejected) by several alternative procedures. Many residues reported in the past could be erroneous because the analyst failed to perform the confirmations. Techniques useful for confirmatory tests are gas chromatography (GC) employing a variety of detectors and/or columns of different polarities, TLC, p-values, derivatization, liquid chromatography (LC), GC or LC instruments coupled to a mass spectrometer (MS), and others. An excellent text which addresses most of the aspects of pesticide residue analysis is that of Moye published in 1981 (36).

Recent advances in the analysis of pesticide residues include increased use of LC, attempted inclusion of polar compounds in multiresidue schemes, greater emphasis on analysis of metabolites and conjugates, development and use of GC-MS systems, and methods development for a relatively new class

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of pesticides, the synthetic pyrethroids (44). Capillary GC is also becoming widely accepted in residue analysis because of the high quality columns now available which yield a high level of resolution and longevity not previously attainable. An example of the highly sophisticated methods now being developed is the isomer-specific determination of 2,3,7,8-tetrachloro-*p*-dioxin (2,3,7,8-TCDD) by capillary GC/atmospheric pressure negative chemical ionization/MS (45). It should be noted that 22 TCDD isomers are possible and many other chemicals such as DDT, DDE, PCBs, toxaphene, benzyl phenyl ethers, and chlorinated methoxybiphenyls have been known to interfere in previous methods; yet in this procedure the 2,3,7,8-TCDD can be specifically determined in tissue at the low parts-per-trillion level. On the other hand, the availability of methodology to determine such infinitesimal levels of residues imposes an almost insurmountable task on toxicologists, i.e., the task to determine their toxicological significance to humans and the environment.

An excellent review of governmental regulations pertaining to pesticides and their residues was presented by Leng in 1981 (46). Pesticide Assessment Guidelines revised in 1982 are available at moderate cost through the Environmental Protection Agency, Washington, DC. Extensive research is now required for pesticides before consideration for registration; therefore, it is anticipated that only effective and safe materials will gain approval in the future.

The members and officials of AOAC can take great pride in the accomplishments of the Association during the past century. Many of the significant accomplishments in pesticide analysis previously cited were first reported as meetings of the AOAC and/or in the *Journal*. Similar accomplishments were simultaneously being made in many other areas of the analytical sciences. The *Official Methods of Analysis of the AOAC* will continue to provide a source of tried and proven methods recognized by government, industry, and the courts. Continued support of the Association by its members and sustaining members, and an even more active participation in the laboratory collaborative process, will ensure the availability of reliable and accepted methods for all of the analytical sciences in the future.

Epilog: A Time Capsule for 2084

With faith that humankind will somehow gain the wisdom to live and work together in peace to allow our civilization to survive and develop, the author of this centennial paper and the members of AOAC (1984) send greetings and congratulations to the members of AOAC in their bicentennial year (2084). The current rapid development of electronics, computer science, communication and information systems, and space-age technology in general, makes it impossible for us to even imagine what the state-of-the-art in pesticide science will be a century from now. Undoubtedly, your technology will be highly sophisticated compared with ours. We sincerely hope that you have achieved a high quality of life, and that most of the problems related to the analysis and use of pesticides and all biologically active substances are solved.

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