Meetings

Analytical Chemistry in Nuclear Technology

Developments in instrumental methods of analysis were the main topics of discussion at the 7th Conference on Analytical Chemistry in Nuclear Technology, held in Gatlinburg, Tennessee, 8–10 October 1963. The discussions were slanted primarily toward the needs of the nuclear analytical chemist: the analysis of molten salt systems at high temperatures; the utilization and standardization of instrumental devices in nuclear analysis; spectroscopy in its broadest aspects; gas chromatography; electroanalytical chemistry; and the automation of all such methods, procedures, and devices where it is practicable or desirable to do so.

Approximately 300 interested scientists, including 30 analytical chemists or instrumentation experts from 11 different foreign countries, participated in the conference either by presenting one or more of the 50 papers that were given or by engaging in the two panel discussions.

The first panel discussion was, in fact, a continuation of a meeting which was held on the day preceding the conference by a Sub-Committee of the National Research Council on the problem of the availability, development, and use of radioactivity standards. The interrelationship and interdependence of absolute activity measurements, half-lives, and beta- and gamma-ray-branchings were never more clearly delineated than they were in this panel discussion. The recurring thought, which was reemphasized by questions and comments from the audience, was the basic need of the importance of knowing and using best values for these nuclear parameters. A second point frequently mentioned was the significance of differentiating between when absolute measurements, and hence accurate standards, are necessary and when relative measurements are sufficient. The panel of experts included: S. B. Garfinkel (National Bureau of Standards); G. I. Gleason (Abbott Laboratories); H. Houtermans (International Atomic Energy Agency); Bernd Kahn (U.S. Public Health Service); D. S. Kim (Nuclear-Chicago Corp.); J. G. V. Taylor (Atomic Energy of Canada Limited); and the moderator, W. S. Lyon (Oak Ridge National Laboratory). They discussed the present state of standardization techniques, areas for future research, and the immediate and long-term needs for standards. It was reported that the National Research Council Sub-Committee on the Use of Radioactivity Standards has under way several projects which will alleviate some of the present difficulties in the use of standards. These projects include the compilation and publication of best half-lives, decay schemes, gamma branchings, and conversion coefficients for many of the more commonly used radionuclides, and also the publication of a user's guide of radioactivity standards. Research work at Chalk River, Oak Ridge National Laboratory, and other institutions directed toward the accumulation of better values for these nuclear data was also reported. The number and types of radioactivity standards available are expected to continue to increase, judging from reports of proposed expansions in the programs of standards distribution at the National Bureau of Standards, Nuclear-Chicago Corp., and the International Atomic Energy Agency.

The second panel discussion dealt with recent developments in analytical instrumentation, emphasizing the attitude and philosophy of the analytical chemist in regard to the acquisition of the knowledge of the principles on which instrumental devices are constructed and utilized. In selecting the panelists, an effort was made to include experts proficient in different aspects of instrumentation. Each of the panel members spoke for a short time on a subject of his own choice relevant to the general topic of the session. After the first three presentations, and again at the end of the session, the meeting was thrown open for discussions by the panel and for participation of the audience. G. Milazzo (Rome) led off the discussion with a description of his work with a hollow cathode light source for the spectrographic determination of nonmetals. He also described a vacuum ultraviolet spectrograph that was designed to measure the emission characteristics of these elements in the far ultraviolet. He revealed that 10^{-7} to 10^{-8} gram of iodine could be detected in this manner. H. V. Malmstadt (Illinois) told about his efforts to develop an understanding of electronics by chemists and other scientists and thus remove some of the mystery about the "black boxes." He has developed a laboratory for experimental work in electronic circuitry which makes use of simple units, power supplies, operational amplifiers, and other components which can be interconnected with suitable networks fitted with clips, so that several types of circuits can be studied in a short time. C. W. Weber described some of the unique gas analysis instruments that have been developed at the Oak Ridge Gaseous Diffusion Plant (ORGDP) and which are based on the use of very sensitive differential pressure transmitters, such as a continuous gas titration analyzer and a condensation pressure analyzer.

H. I. Shalgosky (England) presented some of his ideas on analytical instrumentation and expressed the thought that chemists should be able to communicate and cooperate closely and intelligently with instrumentation engineers in designing and utilizing instrumental devices. H. M. Davis (England) formerly worked with Shalgosky and agreed fully with him on the relationship between the chemist and design engineer. As an example of the greater adequacy of instrumentation developed as a consequence of this philosophy, he cited the integrating flame photometer, a device of very high sensitivity which was designed at the Woolwich Outstation of the United Kingdom Atomic Energy Authority (UKAEA).

H. M. Kelley (DuPont) described some of the instrumentation in use in the laboratory of the Savannah River Plant of the U.S. Atomic Energy Commission. He cited the scanning coulometer as an instrument suitable for the highly precise analysis of small amounts of reducible substances, such as uranium and plutonium. He described the application of the Technicon Autoanalyzer to laboratory problems but also stressed the importance of not overemphasizing the completely instrumental approach to analytical problems. G. L. Booman (Phillips Petroleum Co., Idaho Falls, Idaho) advocated the applications of the principles of cybernetics to the design of instruments and to automatic control systems. In designing instruments involving the use of operational amplifiers, he emphasized the advantages that may be gained by experimentally measuring the transfer function or functions of the system rather than by using a more empirical approach.

In the first general session of the conference, H. A. Laitinen (Illinois), one of the first to apply electroanalytical measurements to molten salts at high temperatures, reviewed methods for purifying molten mixtures, the construction of reference and indicator electrodes, and materials of construction. Voltammetry, chronopotentiometry, coulometry, cuolometric titrations, and impedance measurements were also discussed. Laitinen used the complicated reduction of V_2O_5 in LiCl-KCl to illustrate the advantages of two or more types of measurements on a particular solution. L. C. Hall (Vanderbilt) reported on a third order disproportionation of $EuCl_3$, $YbCl_3$, and $SmCl_3$ in a molten mixture of LiCl and KCl. Computer programs are being tested to evaluate the forward and backward reaction rates. Gleb Mamantov (Tennessee and ORNL) reviewed the voltammetric and chronopotentiometric studies of molten mixtures of LiF, NaF, and KF and of LiF and BeF_2 which are being carried out at Oak Ridge. Current-voltage curves and potential-time curves were discussed for iron, nickel, uranium, and zirconium for systems in which pyrolytic graphite sheathed in boron nitride was used as an indicator electrode.

In the area of optical measurements, D. M. Gruen (Argonne) discussed electronic absorption spectroscopy both as an analytical tool and as a means of elucidating oxidation states. Gruen also pointed out that transition-metal ion spectra (octahedral-tetrahedral transitions) provide an important insight to melt structures. W. T. Carnall (Argonne) reported on spectrophotometric studies of lanthanides and actinides in a molten mixture of $LiNO_3$ and KNO_3. It was reported that absorption bands in the 1.4- to 2.6-micron region correlate with predicted bands in this area and that transitions of highly radioactive promethium and curium were observed in melts stable to radiation. J. R. Morrey (Hanford) described furnaces which were designed for use with the Cary Model 14 spectrophotometer. Spectra of U(III) and U(IV) in fused chloride were presented as examples of solvent effect on the spectra of the solute. Specialized techniques for spectrophotometric studies of molten fluorides were discussed by J. P. Young (ORNL). Of special interest in his talk was the description of a new high-temperature cell assembly and a unique "windowless" sample holder.

At the sessions on instrumentation and techniques for nuclear analysis, Peter Crowther (South Africa) and J. S. Eldridge (ORNL) reported on a number of inconsistencies that appear in published decay schemes of radioactive nuclides and told how intercomparison measurements by beta-gamma coincidence counting, $4\pi\gamma$ ionization counting, and absolute NaI gamma-ray spectrometry have yielded more reliable gamma branchings for a number of radioactive nuclides. S. B. Garfinkel (NBS) outlined the techniques used in the standardization of electron-capture nuclides. Of particular interest is the sum-coincidence method, used for I^{125}, in which the singles and coincidence sum peaks from the K x-rays of I^{125} are measured by gamma-ray spectrometry. A. Chetham-Strode and J. R. Tarrant (ORNL) described the use of solid-state detectors and presented recent evidence of great improvements in the resolution of the Frisch grid ionization chamber through use of mixed-gas fillings. Resolution of 16 Kev at 2π geometry has been observed with alpha emitters in the uranium series. This compares favorably with resolutions obtained with solid-state detectors.

Another session of the conference was devoted to a discussion on instrumentation for the remotely controlled analysis of radioactive materials. One of the problems that has consistently presented difficulty in the analytical chemistry associated with chemical processing of uranium by the Purex process was given a new solution by Kenji Motojima (Japan), who told about a modified alkalimetric method for the determination of free acid and uranium based on the use of ammonium sulfate as a masking agent, and of H_2O_2 for evaluating the hydrolytic equivalent of the uranyl ion. Further refinements in the automation of the remotely operated specific gravity apparatus (falling-drop method) at the Idaho Chemical Processing Plant were described by F. W. Dykes. Specific gravity in the range of 1.00 to 1.40 can be determined routinely on highly radioactive solutions with a standard deviation of 0.0017 unit. Something akin to the "chemist-in-a-box" approach to automatic chemical analysis was described by J. C. Gillespie (Union Carbide Corp., Paducah, Kentucky). He described a simple system where as many as 200 separate events per sample can be programmed in equipment that is operated by laboratory technicians.

Recent developments in in-line chemical instrumentation at the UKAEA Windscale and Calder Works was the topic of J. K. Foreman (England). An automatic coulometric acidity meter, a ferrous sulfamate concentration monitor, and a nitrite detector based upon the color reaction with starch-iodide solution were described. The instrumentation, in addition to providing continuous chemical analysis at a reduced cost, serves as an approach-to-criticality alarm system. A versatile, low-cost, remote-handling system for making chemical analyses designed for use at Windscale was presented by A. J. Howarth (England) (paper read by J. K. Foreman). The system is based on the use of a gantry crane device to handle activities up to 100 curies in fully shielded operations. Analytical methods and remote-handling facilities for the Molten Salt Reactor Experiment and for the Transuranium Program at the Oak Ridge National Laboratory were described by L. T. Corbin (ORNL). Specialized handling equipment and remotely operated instrumental methods which are to be used for the analyses of the materials involved in these two programs were discussed briefly. L. L. Merritt, Jr. (Indiana) described an automatic, electrically controlled analytical balance suitable for remote weighing, and for continuous recording, giving four-digit accuracy for both 0.1- and 0.01-mg sensitivity ranges.

In the session on electroanalytical instrumentation, Irving Shain (Wisconsin) reported on advances that have been made in the theory of stationary electrode voltammetry, particularly the cyclic methods. He expects to publish the results of this work soon. A number of diagnostic criteria were described which characterize the mechanisms of the electrode reactions, including coupled processes. Applications of operational amplifiers in electroanalytical chemistry at the Oak Ridge National Laboratory were summarized by M. T. Kelley (ORNL). He reported that operational amplifier systems have been used extensively for a wide variety of purposes, including potentiostatic and galvanostatic electrolysis, current integration, time derivative computations, impedance matching, voltage inversion, d-c or tuned a-c voltage gain, current amplification, and end point detection. Milazzo (Rome) presented a paper on the design and performance of an automatic electrometric titrator in which a delay circuit was described which prevents final stoppage at premature end points in slow reactions. He stated that this titrator can be used either manually or automatically with very good performance in potentiometry and amperometry, and with the addition of certain accessories can also be used satisfactorily in conductometry and coulometry.

H. I. Shalgosky (England) spoke on the technique of, and results obtained by, high-precision, comparative polarography with the Davis Differential Cathode Ray polarograph. When the cells contain solutions of nearly the same concentration, one being a reference standard, the species in the other cell can be determined with very high precision. H. M. Davis (England) described the design features of a new instrument, the prototype of which was developed by Davis and others at Harwell. The mechanism for synchronizing the drops is of advanced design. High sensitivity and resolution were reported. The instrument can be used in the subtractive mode with either base electrolyte and reagent blank or with a standard solution in the reference cell or for derivative display. This polarograph can be used for single cell methods.

H. L. Pardue (Purdue) related the details of an automatic method for measuring the slope of kinetic curves including a discussion of the principles of a servo, direct-reading instrument. He also gave some examples of the utility of this method in measuring concentrations of certain organic compounds in the ppm range. T. M. Gayle and T. A. Gens (ORNL) described the instrumentation for the continuous detection of hexavalent chromium for use in the control of a DAREX process. They found that methods based on oxidation potential were more satisfactory than those methods based on ultraviolet absorption in the continuous monitoring of a DAREX dissolver effluent stream.

Mavrodineanu (Philips Laboratories), coauthor of the first comprehensive textbook on flame photometry, led off the discussion on spectroscopy by describing some of his recent investigations of excitation phenomena in premixed flames. By using specially constructed burners which produced widely separated inner and outer cones, he was able to secure greatly enhanced emission of some species and total suppression of others. When the nitrogen in the air fed to pre-mixed air-acetylene flames was replaced by argon, the spectra showed little change, indicating that the role of nitrogen in this flame, if any, was not a chemical one. He suggested the use of the term "overexcitation" rather than "chemiluminescence" to cover the phenomena responsible for the presence of hard-to-excite lines in flames. R. C. Hughes, of the same laboratory, described a four-channel, direct-reading Fery prism spectrometer being developed especially for use with flame sources. He reported that the device has a single readout unit, with digital display, which can be switched to the tubes in sequence. As a method of volatilizing solutes for atomic absorption analysis, flames have the disadvantages of turbulence, inherent absorption bands, and unwieldiness. J. P. Mislan (Canada) showed that the passing of an aerosol of a cadmium solution through a quartz tube furnace will produce detectable absorption below the level of 0.03 μg/ml. The speaker hoped to adapt this approach to on-stream analysis.

R. S. Vogel (Mallinckrodt Chemical Works) described a meticulously carried out investigation in which he obtained emission spectra of sample areas 5 to 10 μ in diameter by refinement of the point-to-plane technique. A paper by A. G. Collins and C. A. Pearson (Bureau of Mines) related the details of an acetyl acetone extraction-emission spectrochemical technique for determining beryllium in oilfield waters. R. N. Whittem (Australia) talked on the construction of a spectrographic device for monitoring beryllium in paper smear samples. A paper by S. Hanamura (Japan) illustrated the advantages of signal integration in overcoming the noise problems encountered in determining magnesium and sodium by flame photometric methods.

At the final session, David Bandel (Bendix Corp.) discussed the high degree of resolution of a Hypeac interference spectrometer and related how the improvements which have been made in utilizing a sealed-source, hollow-cup cathode discharge tube for the excitation of samples has made this instrument readily adaptable to the analysis of radioactive materials without requiring a prior chemical separation. This instrument has been used to measure lithium, plutonium, and uranium isotopic abundances on samples ranging in size from several milligrams to 2 or 3 grams. The U^{235}/U^{238} ratio in natural uranium can be measured to within ± 1 percent. P. J. Bourke (England) presented a paper on the gas chromatographic determination of impurities in helium down to a fractional part per million by utilizing a sensitive ionization detector to measure concentrations as low as 0.02 ppm of CO_2, 0.05 ppm for CO, with decreasing orders of sensitivity for oxygen, argon, nitrogen, and hydrogen.

B. D. La Mont (Westinghouse Electric Corp.) discussed methods for the analysis of uranium carbide, for total carbon, free or uncombined carbon, oxygen, nitrogen, and hydrogen. Total carbon is determined gravimetrically after combustion in oxygen. Free or uncombined carbon is also determined gravimetrically after selective dissolution of combined carbon and uranium with nitric acid. For the determination of oxygen and nitrogen, uranium carbide is reacted with BrF_3 at room temperature, thus releasing combined oxygen and nitrogen as elemental gases, which are then determined by gas chromatography.

Contrary to the precedent established through the first six conferences, the proceedings of this conference will not be published, but some of the papers will undoubtedly be published in the open literature.

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