Analytical Chemistry in Nuclear Technology

The chemist engaged in analysis of high-purity nuclear and reactor materials, especially for substances present in concentrations of parts per million or per billion, is faced with a number of problems. Among the most important of these is that of knowing exactly what information about the composition of the material in the reactor is needed by the engineer requesting the analysis. Especially difficult is the problem of choosing a method or methods of analysis which will yield information of requisite accuracy and precision in a reasonable time and at reasonable cost.

An outline of these problems and suggestions for solving them were presented by A. A. Smales of the United Kingdom Atomic Energy Authority, Harwell, England, at the eighth Conference on Analytical Chemistry in Nuclear Technology, held 6–8 October 1964 in Gatlinburg, Tennessee. Smales pointed out that the analytical chemist in selecting the most appropriate method of analysis must consider advantages and disadvantages of each possible method. He briefly evaluated a number of different methods, including absorption, fluorescence, and emission spectroscopy, gas chromatography, mass spectrometry, isotope dilution, vacuum spark, resonance spectrometry, and radio activation analysis, with regard to their sensitivity, specificity, accuracy, and freedom from contamination. He stressed that a competent analytical chemist must be quick to learn and evaluate new techniques and be willing to adopt them where suitable. Smales indicated a great interest in the utilization of the techniques of spark-source mass spectrographic instruments of recent design, which he thinks promise to alleviate the problem of trace analysis of high-purity metals. These instruments were discussed earlier in the conference by W. Fletcher (UKAEA, Capenhurst Works) and J. C. Fletcher (Y-12 Plant, Oak Ridge, Tennessee).

To the question of whether he thought the so-called "wet chemist" will disappear from the analytical laboratory, Smales replied that he did not. He commented, however, that this does not mean that the "wet" methods should be retained when new methods and techniques are more adequate.

Smales also pointed out that planning by the analytical chemist and the engineer who will use the results of the analysis can avoid or circumvent many problems, including those of analysis, during the early stages of development or research work.

In the session on burnup of fuel in reactors, the use of both radioactive (^{99}Tc) and stable (^{139}La) fission product nuclides as burnup monitors was discussed. A handicap to the accurate determination of the degree of burnup is the large uncertainty concerning the values for a number of the physical constants, such as fission yields and cross sections, that are needed in calculating the growth or decay of certain isotopes and their relation to the disappearance, or burnup, of fissionable fuel. J. E. Rein described the long-range program at Phillips Petroleum, Idaho Falls, Idaho, which has as its goal a better understanding of these parameters.

At the session on nuclear methods of chemical analysis, the precision, applications, and differences in techniques of radioactivation methods of analysis were described. At another session general applications of liquid scintillation counting were presented, including a description of a method for determination of noble gases by D. L. Horrocks and M. H. Studier (Argonne National Laboratory) and a technique for absolute assay of beta emitters of maximum energy greater than 200 kev by G. Goldstein (Oak Ridge National Laboratory).

New or modified techniques were discussed in the session on the determination of carbon, hydrogen, oxygen, and nitrogen. M. E. Smith (Los Alamos Scientific Laboratory) told of a device for crushing pyrolytic carbon-coated uranium carbide particles in the inert atmosphere of the furnace prior to analysis for oxygen. M. S. W. Webb (UKAEA, Woolwich) described an apparatus with which 27 steel samples could be analyzed spectrographically for oxygen. The apparatus was sensitive to as little as 1 μg of oxygen, and the analysis time was 2.5 minutes per sample.

W. E. Dallman (Iowa State University) presented data from a comparative study on the determination of gases in rare earth metals. Inert gas fusion, hot extraction, vacuum fusion and d-c carbon arc methods were discussed.

A complete session was devoted to the analysis of trace impurities in the alkali metals. The impurities discussed were oxygen, carbon, and hydrogen. Methods discussed for the determination of oxygen were a modification of the amalgamation technique which reduced the time per analysis, a distillation technique, and a neutron activation method. A freezing-point method for the determination of oxygen in rubidium and cesium was presented. Both wet and dry combustion methods for the determination of carbon were discussed, and thermal extraction and isotopic dilution techniques were presented for the determination of hydrogen. Of note was the application of the modified amalgamation technique to the simultaneous determination of oxygen and hydrogen in the same sample.

The conference was sponsored by the Oak Ridge National Laboratory, operated by Union Carbide Corporation under the auspices of the U.S. Atomic Energy Commission.

C. D. Susano, L. J. Brady
Gerald Goldberg, W. R. Laing
W. S. Lyon
Oak Ridge National Laboratory, Oak Ridge, Tennessee

Space Simulation: Man-Rated Testing and Vacuum Generation

Human beings have been used as subjects in tests in pressure chambers associated with deep-sea exploration and in altitude chambers for simulation of aircraft flight, but "man-rated" testing in the simulated environment of space is in its infancy. Such testing, performed in space-simulation chambers designed for life-support and safety, is required in the development of manned spacecraft and in training for lunar exploration and other extravehicular space activities. Along with the improvement of vacuum systems for space testing, man-rated testing was a principal topic at the second national Space Simulation Testing Conference (Pasadena, California, 16–18 November 1964), sponsored by the American Institute of Aeronautics and Astronautics.

Space-simulation chambers are needed for man-machine tests and to evaluate support equipment: suits, control systems, portable life-support systems, and the like. A manned chamber requires the combination of a reliable vacuum chamber with its associated systems and controls which, in the event of any type of failure or malfunction, can be made to react immediately to produce a safe environment for the occupants. Man-rating of the chamber should be provided for during the design stage rather than by adaptation after completion. Interaction of the various systems must be analyzed and studied in detail to assure overall system compatibility and reliability.

J. Maloney (McDonnell Aircraft Corp.) reviewed man-rating design considerations which governed the design of a chamber for testing the Gemini two-man Earth-orbiting spacecraft. J. Chappee (NASA Manned Spacecraft Center) in a similar paper reviewed and discussed the man-rating considerations that were confronted in designing the Space Environmental Simulation Laboratory which is currently under construction for testing the Apollo manned lunar exploration spacecraft. Maloney pointed up the need for special chamber structure to assure structural integrity under repeated load cycling; philosophies and considerations in specifying and designing manlocks, view ports, lighting ports, doors, and fire protection systems were also covered. Pumping systems employed with man-rated chambers are similar to those used for unmanned chambers, with certain modifications; for example, quick-closing valves are required on diffusion pumps to prevent oil from entering the chamber during emergency repressurization.

An emergency repressurization system is mandatory to protect the occupants should they be suddenly exposed to the vacuum and temperature of the chamber. Such systems are normally designed to achieve automatically a life-sustaining atmosphere (0.34 to 0.4 atm or 5 to 6 lb/in.^{2} total pressure, oxygen partial pressure about 0.27 atm) in about 20 to 30 seconds, with further repressurization of the chamber being manually controlled and programmed as the circumstances may dictate. Other parameters to be considered in designing quick repressurization include the resulting air temperature, noise levels in the chamber, and dynamic pressures or air loads caused by the high rates of flow.

Chappee stated that the "buddy" system, a commonly used rescue or safety technique, is not applicable to man-rated chamber testing since virtually nothing is to be gained by having a second man stand, also in danger, at the first man's shoulder. The full-pressure suit of today greatly impairs mobility and thus reduces the usefulness of the buddy system. Only rarely is a suited observer expected to be useful; observers will be on standby in a manlock and not in the chamber. Continuous medical monitoring of the test subject is a vital consideration in man-rated testing. Complete systems for communications between subjects, chamber operators, and medical monitors are required, and many trial runs are necessary prior to the actual testing.

G. Frankel (Republic Aviation Corp.) reported results of recent manned tests conducted in a space chamber at a simulated altitude of 10,500 m (35,000 feet). The object of the tests was to determine the ventilation efficiency of a prototype space suit for the Apollo program. The subject operated a bicycle ergometer at a constant metabolic rate with variable ventilation flow rates, and at various metabolic rates with a constant ventilation flow rate. Ventilation efficiency decreased with the ventilation flow rate for the range of variables studied. The investigators concluded that a ventilation flow rate of 1.94 lit./sec (4.1 ft^3/min) NTP at an inlet pressure of 0.25 atm will maintain an acceptable mean body temperature indefinitely, within the physiological limitations of dehydration and fatigue, during work generating 363 kcal/hr (1440 Btu/hr). Heat removed by the particular ventilation system studied probably will not be significantly increased by ventilation flow rates greater than 1.89 lit./sec NTP.

Most current space chambers utilize roughing pumps coupled with oil diffusion pumps to achieve vacuums in the range of 10^{-8} to 10^{-10} torr. Cryopumping is often used as a third stage for achieving even lower pressures. The pumping speed of a cryosurface under free molecular flow conditions can be predicted from kinetic theory if the capture coefficients for the various gases present are known. Very little information exists on the capture coefficients of many common gases; essentially none on the cryopumping of gases at high temperatures. J. P. Dawson (ARO, Inc.) reviewed the basic elements of molecular kinetic theory, including the relation of the capture coefficients to the pertinent gas parameters and the experimental pumping speed. The critical-velocity model proposed by B. A. Buffham, P. B. Henault, and R. A. Flinn and F. C. Collins to explain theoretically the effects of gas temperature on the capture coefficient, was used to analyze experimental pumping speeds over a gas temperature range from 77° to 400°K for carbon monoxide, carbon dioxide, nitrogen, argon, oxygen, nitrous oxide, air, and a 90 nitrogen–10 oxygen mixture. For gas temperatures of 300°K and above, the capture coefficient was mainly a function of the gas temperature. Equations developed from the critical velocity model permit the estimation of capture coefficients of most gases if certain physical data on the gas are known or if the capture coefficient is known for one gas temperature.

Cryopumping as currently employed in conventional systems has its limitations in pumping large volumes of hydrogen outgassed by the spacecraft or component under test. E. A. John and W. E. Hardgrove, reporting on recent work in this area at NASA Goddard Space Flight Center, reviewed current pumping technology and pointed up the shortcomings of conventional cryopumping techniques. They proposed incorporation of a cryosorption array into a conventional cryopumped vacuum system to alleviate the limitations of the cryopumping; they used experimental data obtained by S. A. Stern *et al.* at 10^{-6} to 10^{-9} torr on the adsorption of hydrogen on a molecular-sieve material to predict performance of the sieve at 10^{-15} torr and 15° to 20°K. They pointed out that cryosorption at 20°K provides higher pumping speeds than cryopumping at 4.2°K, an obvious economic advantage. A design for a small chamber for achieving vacuums to 10^{-15} torr by use of cryosorption was proposed; however, the limitations of techniques for measuring pressures in this region were noted, and it was suggested that research seek to modify mass spectrometers to permit measurements of partial pressures of hydrogen, helium, and other gases at 10^{-15} torr.

One shortcoming of current techniques for space-simulation testing is the creation of an unrealistic environment by the presence of the test article itself. Outgassing from the test article introduces gases into the chamber, portions of which, depending on the nature and design of pumping system and chamber, are reflected from the chamber walls back to the surfaces of the test article; whereas a vehicle in space is in an environment which provides a near-perfect sink for gas molecules originating from the vehicle. Current and envisioned space simulation chambers for environmental testing of space vehicles utilize large areas of cryogenic surfaces with fairly high molecular-capture coefficients. Molecular fluxes from vehicle to walls occur, and the degree of reflection to the vehicle surfaces is a function of vehicle size, chamber geometry, and cryogenic capture-coefficients for the gases evolved by the vehicle.

C. E. Cheeseman (ARO, Inc.) reviewed earlier studies of molecular kinetics in space chambers and described recent experiments aimed to gain further insight into the effect of molecular kinetics on space-chamber performance and to verify a theoretical method for the prediction of performance. Cheeseman maintained that pressure as conventionally measured is not a realistic means of determining space-chamber performance because of the experimentally verified occurrence of flux gradients over the vehicle surface; he proposed that chamber performance could be more rigorously defined in terms of an equivalent flux altitude. He showed that flux profiles are significantly affected by the presence of a nonpumping area, such as a solar-simulator bank in the chamber wall, and that fluxes mathematically determined on a vehicle compared favorably with those obtained experimentally.

As a solution to the vehicle selfcontamination problem associated with current test techniques, J. B. Stephens (Jet Propulsion Laboratory) discussed in detail the design of a space molecular-sink facility (MOLSINK) which was claimed to be capable of capturing all but four of every 10,000 condensable molecules emanating from a test item 25 cm in diameter. The facility has a specially configured liquid-helium cryopump in conjunction with titanium sublimation pumps and ion pumps to sustain ultrahigh vacuums in the test volume, and mechanical pumps in conjunction with turbo-molecular pumps to rough-pump the chamber and sustain the guard vacuum.

Stuart Giles (Atomics International) approached contamination from another viewpoint, regarding it as contamination of the test article by the chamber and its pumping systems. He cited examples of contamination of components at high temperatures due to poor space-simulation techniques and offered guidelines to be followed in cases where surface effects are important.

Other sessions of the conference treated the topics of instrumentation and data handling, solar simulation, propulsion-system testing, and testing techniques; many interesting and informative papers were presented. A tour of facilities of the Jet Propulsion Laboratory was provided. The quite successful meeting was well attended by many persons active in the field.

A. C. Bond
NASA Manned Spacecraft Center, Houston, Texas

Forthcoming Events

February

1–2. **Protein** Conf., 19th annual, Rutgers Bureau of Biological Research, New Brunswick, N.J. (J. H. Leathem, Rutgers Univ., New Brunswick)

1–3. Solid Propellant **Rocket** Conf., American Inst. of Aeronautics and Astronautics, Washington, D.C. (D. L. Raymond, AIAA, 1290 Avenue of the Americas, New York 10019)

1–3. **Myasthenia Gravis,** conf., New York Acad. of Sciences, New York. (NYAS, 2 E. 63 St., New York, N.Y. 10021)

1–4. **Information Storage and Retrieval,** American Univ., Washington, D.C. (American Univ. Center for Technology and Administration, 2000 G St., NW, Washington 20006)

1–4. **Solar Atmosphere** Seminar, U.S.–Japan Cooperative Science Program, Honolulu, Hawaii. (Office of Intern. Science