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William E. Collins CNI Aviation, LLC Ada, OK 74820

Michael E. Wayda Civil Aerospace Medical Institute Federal Aviation Administration Oklahoma City, OK 73125

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## **Historical Vignette**

## FIRE AND SMOKE: IMPROVING AVIATION SAFETY THROUGH COMBUSTION TOXICOLOGY RESEARCH

By William E. Collins, Ph.D., and Katherine Wade, M.L.S.

HE HISTORICAL VIGNETTE that follows captures more than two decades of research accomplishments of a biochemistry research team within the Aviation Toxicology Laboratory in the Civil Aeromedical Institute (CAMI). For context purposes, the Toxicology Laboratory (one of several laboratories that originally constituted CAMI's Aeromedical Research Branch) has always comprised a group of research teams identified primarily by their specialty functions. In 2001, CAMI was renamed the Civil Aerospace Medical Institute, and the Toxicology Laboratory became the Bioaeronautical Sciences Research Laboratory.

The vignette represents a self-initiated summarization by Donald Sanders, a research chemist, who developed the material during the 1980s and early 1990s. Its purpose was a means of orienting new laboratory employees on the research activities of Sander's team during the period between 1970-1992. We became aware of the document as a result of publishing a Milestone report of CAMI research in 2005 (DOT/FAA/AM-05/3) when Sanders, who has remained in contact with CAMI personnel since his 1997 retirement, commented that he had prepared some historical material years ago. After reviewing his manuscript, we planned it for inclusion in this issue of the Index, a vehicle previously used to capture historical vignettes, and added some photo documentation.

Donald C. Sanders earned B.S. and M.S. degrees in chemistry from Oklahoma State University and was an instructor there prior to joining CAMI in 1963. His early assignments involved biochemical research on biocidal additives to aircraft

fuels (additives that prevented bacterial and fungal growth in the fuel-water interface of the tanks) and issues associated with the exposure of agricultural pilots to the pesticides they used in spraying fields. The latter was an area of particular emphasis in the Toxicology Laboratory during the 1960s. In 1972, Sanders and two long-term associates, John Abbott and Boyd Endecott (both research chemists), began their exploration of combustion toxicology problems in the aviation environment. The team was headed by Charles R. Crane, Ph.D., a biochemist with degrees from the University of Oklahoma (B.S. and M.S.) and Florida State University (Ph.D.). Crane, an assistant professor at Oklahoma State University prior to joining CAMI in 1961, retired in 1988 and was replaced by Arvind K. Chaturvedi in 1990. Chaturvedi obtained his Ph.D. from Lucknow University, India, and had taught at Vanderbilt University and at North Dakota State University.

During the 5-year period from the end of his historical summary to his retirement from federal service, Sanders (along with Endecott, who retired in 2000) remained a part of the new Biochemistry team where he addressed new tasks including drug/altitude effects and aeromedical aspects of melatonin. He also continued his work on combustion toxicology problems with an emphasis on determining coefficients that would allow prediction of time-to-incapacitation for various mixtures of carbon monoxide and hydrocyanic acid — the principal toxic gases produced by fire in aircraft cabins.



Sander's initial research at CAMI included studies of a biocidal boron-containing additive for aircraft fuels (left) and of plasma-cholinesterase levels in agricultural pilots (crop dusters) exposed to organophosphate pesticides (right).



# Combustion Toxicology Research in the Biochemistry Research Unit, CAMI, 1970-1992

By Donald C. Sanders

## **BACKGROUND**

In the early 1960s, aeromedical scientists became aware of the possible significance of smoke toxicity to survival in postcrash aircraft fires. It was observed that some victims with no impact-related physical injuries died as a result of the ensuing fire. The inevitable questions arose as to what killed them, how could this be proven, and how could this risk be reduced or even prevented in future crashes. The Civil Aeromedical Institute's (CAMI's) Forensic Toxicology Unit, within the Aviation Toxicology Laboratory in the Aeromedical Research Branch, found that victims from such fire accidents invariably had elevated blood carboxyhemoglobin (COHb) levels, indicating inhalation of carbon monoxide (CO) from the fire. In early 1969, the Biochemistry Research Section (then a "unit" comprised of Charles Crane, Ph.D., and a staff of Donald Sanders, Boyd Endecott and John Abbott) became interested in the observation that such COHb values ranged from 35 to 85 percent saturation levels. The obvious questions were: What is the minimal lethal COHb value, and, if CO was not responsible for the death of victims below such values, why did they die? Since there was a possibility that some of the reported COHb values might be in error, our first investigation was an evaluation of the analytical techniques commonly used in standard forensic toxicology laboratories. We found that for postmortem analysis under anything less than ideal conditions, the use of the established colorimetric procedures could introduce considerable error. A substitute gas chromatographic technique was therefore recommended.

## A PROGRAM OF BASIC STUDIES

CAMI's Biochemistry section became directly involved following an impact-survivable accident at Anchorage, Alaska, in 1970. A Capitol International Airways DC-8 had crashed on takeoff (1), and blood specimens from the victims of the ensuing postcrash fire were found to contain cyanide (2). We then undertook a systematic study of the inhalation of both CO and hydrogen cyanide (HCN), using experimental laboratory animals, to establish some basic relationships for these gases. Although it was now recognized that CO was a probable cause of death in smoke inhalation, the emotional

impact of discovering highly toxic **cyanide** in the blood of accident victims affected public opinion enough to require actual research into its origin in aircraft fires.

At that time, little was known about the potential of various aircraft interior components for producing toxic combustion gases in a fire. It was surprising that little documented data existed pertaining to the relative human toxicity of the individual combustion gases themselves. The existing analytical methods, particularly for HCN, lacked specificity, sensitivity and/or reproducibility. Questions regarding the concentrations of CO and HCN produced in aircraft fires and their relationship to the postmortem findings of blood cyanide and carboxyhemoglobin remained essentially unanswered.

Our first animal study was a joint project with Wright-Patterson Air Force Base in Ohio to determine 5-min LC<sub>50</sub> (a dose lethal to 50% of those exposed) values for CO and HCN and to analyze tissue cyanide levels in rats exposed to these specific concentrations of HCN. The resulting analyses convinced us that the then-current methods for measurement of tissue cyanide were completely inadequate. We therefore modified a gas chromatographic detector (converted a flame ionization detector to a nitrogen-phosphorus detector) and developed a method for HCN determination that exceeded the existing colorimetric, fluorometric, and specific electrode standards for specificity and sensitivity. Research in 1970-1972 was devoted to developing methods for determining CO and HCN in chamber atmospheres and in the blood of exposed animals, developing suitable standards for hemoglobin determination, and studying the effects of blood storage conditions on COHb and cyanide content. During 1973, we further refined our sampling and analytical techniques and looked briefly at rhodanese inhibitors to improve storage stability of HCN in blood and tissue samples.

Finally, in early 1974, we began our first in-house rat exposures to HCN, using a 205-L chamber designed by the section personnel and built in the Civil Aeromedical Institute shop. The chamber employed insert cages for LC<sub>50</sub> determinations and less conventional, motor-driven rotating cages for the determination of incapacitation. Our approach to the measurement of combustion gas effects differed from that of conventional toxicologists in that we realized that

the widely accepted  $LC_{50}$  values were of limited application when estimating escape time from a fire environment. We required the definition of the time dependence of the toxic gases on living organisms. We elected to look for the occurrence of psychomotor failure, or physical incapacitation, as our principal endpoint, because that would signal the end of an individual's effective efforts toward unassisted escape from an aircraft. A second deviation from convention was the decision not to count the numbers of rats incapacitated or expired in an arbitrary time period, but to measure the interval between the beginning of exposure and the occurrence of incapacitation or death for each rat (3).

For these initial studies, HCN was generated **in situ** by mechanically injecting a sodium cyanide solution into stirred 10% sulfuric acid inside the chamber. CO exposures were accomplished by injecting commercially available 100% tank CO into the chamber with a 2.8-liter "syringe" of our own construction. By the end of March 1974, we had performed triplicate exposures to CO, to HCN, and to a CO-HCN mixture. These early studies, although crude by today's standards, did serve to justify our choice of a physiological end point; time-to-incapacitation (t<sub>i</sub>) occurred at a fraction of the corresponding time-to-death (t<sub>d</sub>).

During the following six months, we continuously refined our exposure methodology and analytical techniques, investigated gender-related susceptibility (in rats) to CO and HCN, and performed parallel analyses for HCN by colorimetric and gas chromatographic methods. Two important applications were developed during that period. First, the "dose" for the purpose of defining dose-response relationships in inhalation toxicology, is historically defined as the concentration of the gaseous agent plus an additional parameter, the time over which the exposure takes place. By integrating the area under our concentration-vs-time curves from zero to t, we were able to define a "dose," actually a concentration-time product, that was related to a specific t. The second application utilized Guyton's relationship of minute-respiratory-volume (MRV) to animal weight in different animal species (4). Assuming that an incapacitating "dose" would be the same for rats of equal weight and that dose, divided by the animal weight, would give us the incapacitating dose per unit of body weight, we developed an equation relating dose, concentration, time, and weight of the animal. Thus, an incapacitating dose, D, could be expressed as  $D = [C \cdot t \cdot MRV]/Wt$ , where C = concentration in ppm, t = t<sub>.</sub>, MRV = minute respiratory volume in cm<sup>3</sup>/min, and Wt = animal weight in grams (5,6). The equation was equally valid for changing concentrations if the Cot product for the integrated area between zero and t, were used to replace C and t in the formula. This provided the capability to predict biological responses between species for

toxic gases whose mechanism of action was a stoichiometric reaction with critical tissue elements, and hence proportional to total body mass. More pertinent was the exciting possibility of comparing research on nonhuman species to the limited data on human exposures to combustion gases. For CO at least, our calculated physically incapacitating dose for a human, as extrapolated to a 70-kg rat, agreed with the dose predicted by Peterson and Stewart (7) for human acquisition of a 46.5% COHb saturation (8).

## A SHIFT TOWARD MATERIALS TESTING

Initially, our research had been directed toward determining basic information about individual combustion gases. The eventual goal was aimed at converting speculative observations into predictive science. Then, in late 1974, the FAA's Office of Aviation Medicine requested that we attempt to assess the relative toxic potential for numerous aircraft interior materials by exposing animals to their pyrolysis products. The request stipulated that the pyrolysis system be similar to one employed at the FAA Technical Center in New Jersey (now the William J. Hughes Technical Center) to allow correlation of our biological findings with the chemical analysis of pyrolysis mixtures to be accomplished by the Technical Center scientists.



This test exposure by Endecott was performed with CAMI's small, flow-through tubular furnace.

In designing our own system (8), we drew heavily on our previous experience with pure gases. Chamber volume was kept at a minimum to reduce the quantity of sample material needed. The isothermal heating regimen was sufficient to ensure thermal degradation of all organic components in the samples (600°C), and the combustion products were rapidly conducted into the exposure chamber. Oxygen concentration in the chamber was maintained above 90% of ambient, and

the temperature was maintained below 35°C. We selected a maximum exposure period of 30 minutes to keep the carbon dioxide concentration below 5% and to minimize the effect of metabolic detoxification on animal response.

Over the course of the year, beginning in mid-1975, we performed triplicate tests on 75 aircraft interior materials and rank-ordered them based on relative t<sub>i</sub> and on t<sub>d</sub>. We investigated changes in relative rank order when t, and t, response times to equal material weights were compared to the orders obtained when rearranged to reflect the loss of equal weights during pyrolysis. We also calculated response times corrected for both differences in animal weights and sample weights to define the merits of selecting one system over another for a specific application. We compared different materials within their functional types, i.e., foams, insulations, elastomers, etc. Overall relative standard deviation for the t<sub>i</sub> responses for all materials was 13-14%, thus proving the reproducibility of the system for making toxicity measurements of gaseous environments, although the thermal decomposition process did not necessarily represent the actual processes existing in a "real" fire.

Testing the 75 materials proved to be a true learning experience. We had shown (to ourselves, at least) that bioassay could produce very precise endpoints. Deviation from the mean value for 9 rat responses was usually less than 5%, even though individual groups of 3 rats were exposed a month or more apart. It appeared that animals exposed to the same mixture of toxic products on successive occasions reacted the same, and that extreme deviations were related to variations in the combustion process. Materials producing extremely variable results were usually composites, such as layered panels or mixtures of non-uniform composition, that offered sampling difficulties. It was apparent that we had inadequate knowledge about the dynamics of combustion. While we suspected that both the rate of generation and composition of combustion gases would vary with the temperature, oxygen supply, and presence or absence of an ignition source, we had little hard data from the fixed set of conditions imposed on the previous study.

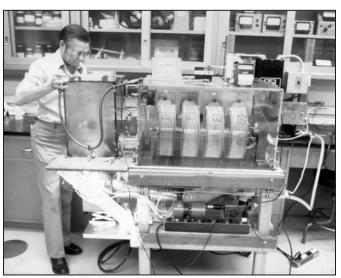
Our next major effort was directed toward developing a new combustion system where sample heating could be programmed, airflow could be controlled over the decomposing sample, and a controllable ignition source could produce flaming or non-flaming combustion as desired. Concurrently, we pursued research to identify the variables of a small-scale test for toxicity. The variables included such diverse factors as effects of carbon dioxide inhalation on breathing rate (and its subsequent effect on t, when combined with other toxicants), preliminary animal exposures to hydrogen sulfide and sulfur dioxide, and the determination of minimum t,s

from high concentrations of CO and HCN to further refine our equation for the describing  $t_i$ -vs-concentration curves. We also developed a smoke detection unit for the combustion system that would record smoke density-vs-time during individual material tests.

In 1977, the Biochemistry Section began a study of the toxic potential of 14 state-of-the-art insulating materials for electrical conductors sponsored by the Urban Mass Transportation Administration (9). These materials were selected from a larger group of insulations being evaluated by the Boeing Commercial Airplane Company for properties other than toxicity. Although we determined rat response per unit weight of insulation, we normalized the data to response per unit length of conductor to permit comparison of insulated conductors on the basis of their intended end use. This study utilized our modified 2-inch diameter combustion tube, wrap-around heating units, and a spark igniter. The system allowed us to investigate differences in animal response times to combustion gases produced during three different heating conditions: 1) low-temperature, nonflaming; 2) low-temperature flaming with hot-wire ignition; and 3) high-temperature, flaming at 750°C with or without ignition. Differences in response times noted at different combustion conditions prompted the proposal that materials should be tested at several conditions and ranked on the "worst case performance" found.

## **OUR INFLUENCE EXPANDS**

During this period (1977-78), section personnel participated in a National Bureau of Standards (NBS) ad hoc committee effort to devise and evaluate a small-scale animal



CAMI's large, rotating cage chamber with a "Potts" furnace was used by Crane for this gas exposure test.

test procedure that could be recommended for identifying materials capable of producing "unusually" toxic combustion products. This effort evolved into an inter-laboratory study in which eight different laboratories separately evaluated a control set of standard materials for their combustion toxicity and compared results. Participation in this evaluation required that we modify our 205-L chamber, previously used for pure gas studies, to accommodate a "Potts furnace" combustion unit in an attached chamber, to develop insert chambers for rats that would allow head-only exposure, and to build a "leg-lift" shock avoidance device to measure the specified incapacitation response. The final protocol was adopted in January 1980; our laboratory participation in the cooperative study was concluded in June of that year. The study, although informative, was not conclusive. The published method (10) was used to compare materials on the basis of the toxicity of their combustion products and modification of the method (11) was recommended "for research and preliminary screening purposes."

The ranking of materials by the original method (10) was generally opposed by the plastics industry. It should be remembered that many, if not most, of the researchers who were participating in method development during that period were associated with the wood and plastics industries. Vested interests influenced many of the suggested cut-off levels for determining "unusually toxic" materials; suggestions of "more toxic than the principal product of the company represented" were common. This concern was not entirely unwarranted. A generally accepted test method, perhaps legally enforced, that indicated the superiority of one product over another, could have a devastating effect on manufacturers of the lesser product. Such an outcome would be clearly unfair if the laboratory test method were not (or could not be) validated by corresponding tests in a large-scale fire.

While participating in the NBS cooperative study, we continued to test some state-of-the-art materials that showed promise for use in aircraft interiors and to perform combustion toxicity tests on a variety of materials when requested by outside agencies. These included foam mattress material from a Columbia, Tennessee, jail fire that killed 42 people, Proban-treated wool for the Civil Aviation Attaché to the British Embassy, safety slide material for the American Safety Equipment Company, and rocket propellants for the Thiokol Chemical Corporation. Our research during 1978 was directed toward establishing the thermal tolerance limits of rats and mice subjected to acute exposures at elevated air temperatures. For this limited study, we built a heated and insulated chamber, equipped with a rotating cage assembly, to evaluate the undefined effects of thermal stress on the rats commonly used in combustion toxicology research (12). Dr. Charles Crane also investigated the limited data on human tolerance limits to elevated temperature and proposed rationales for predicting human escape time in rising temperature environments (13) and predicting human tolerance limits to systemic toxic gases (14, 15). Speculative correlations were made between human incapacitation and postmortem COHb/blood cyanide findings in fire-related aircraft accidents (16).

During 1978-1979, Dr. Crane participated in the discussions of the Special Aviation Fire and Explosion Reduction (SAFER) Committee established by the FAA's Flight Standards Service to recommend ways to improve survivability in post-crash environments (17). This committee, and its individual working groups, represented government, industry, and academia. Recommendations for both short- and long-term solutions for post-crash fire hazard reduction and selection of compartment interior materials were extensively discussed.

## **IRRITANT GAS STUDIES BEGIN**

By mid-1980, we began preliminary studies of irritant gas effects. Hydrogen chloride (HCl) gas is a major decomposition product of halogenated polymers such as polyvinyl chloride and polychloroprene used wiring insulation, seats, and fabrics (18). Initial experiments indicated that we would need a high flow rate of HCl gas through the chamber to maintain a fixed concentration due to the extreme solubility of the gas in aqueous (body) fluids. We built a small (12-L) chamber with an enclosed motor-driven rotating cage, adapted a colorimetric method for quantitating gaseous HCl, and determined the t<sub>i</sub> and t<sub>d</sub> responses by a series of single rat exposures. Individual rat tests were necessary for wholebody exposures because equilibrium concentrations could not be maintained using multiple animals. The HCl (gas) concentrations required to produce incapacitation proved markedly greater than those reported in the scientific literature of that period and suggested that the literature values for humans might have been based on discomfort indices instead of actual incapacitation (18). We were also able to modify another chamber to allow head-only exposures to HCl (gas) in multiples of four rats/test to examine delayed deaths following fixed time/concentration exposures. This chamber also enabled us to remove animals immediately following death for COHb analysis after exposure to CO and to CO-HCl gas mixtures.

Our modest success with the HCl (gas) study encouraged us to consider another irritant gas, acrolein, that had been reported as a combustion product of certain materials used in aircraft interiors. In March through May of 1981, we developed a gas chromatographic method for acrolein determination in air and confirmed it by a separate colorimetric analysis. Rat exposures, in the following two months, indicated that concentrations required to produce incapacitation were also greater than those suggested by the scientific literature; equations were derived from our empirical data to allow prediction of t<sub>1</sub> and t<sub>d</sub> for the laboratory rat (19). It should be noted that our approach to the study of the biological responses to each of the combustion gases included a quantitative mathematical correlation between concentration and response time. We considered that if combustion toxicology was to become a predictive science, this kind of correlation would allow chemical analysis of smoke with subsequent computer modeling to gradually replace rat exposures as a measure of toxicity.

In mid-1981, several accidents involving turboprop aircraft occurred that were believed to have resulted from pilot incapacitation from toxic fumes introduced through the cabin pressurization system. It was alleged that a broken carbon seal in the engine would allow lubricating oil to enter the air compressor section, allowing oil-contaminated air to enter the cabin and causing a degradation of pilot performance. We initiated a study of the effects of the thermal decomposition products of selected petroleum-based and synthetic lubricating oils. We also examined exposure to aerosols of one synthetic lubricant and of paraffin oil. We found that none of the products generated smoke components significantly more toxic than the quantity of CO produced, which, in the engine tests, was reported to be insignificant (20). It also marked our only experience with the laboratory generation of aerosols for animal exposure studies.

Beginning in late 1981, we were requested by the Transportation Systems Center (TSC) to evaluate the toxicity of the thermal decomposition products from six electrical wiring insulations selected from a group of candidate materials by Factory Mutual Research of Norwood, Massachusetts. Evaluation was by the methods used in the 1977 study (9), and a composite ranking for these and the 14 materials in the earlier study was prepared at the request of the TSC technical monitor (21). One additional "halogen-free" wiring insulation was also tested using this method.

The wiring insulation study took up most of the section's activity in 1982. Between material testing sessions, we evaluated soot penetration into the respiratory system of the rat when exposed to smoke from burning polyvinyl chloride pipe. We also found that rats with artificial nasal obstructions were incapacitated by HCl in about half the time required for control rats. A preliminary look at species differences was obtained by exposures of gerbils to CO and to the gases from a modacrylic fabric (a known CO and HCN producer).

Another inhalation toxicology related problem was investigated in 1982 at the request of the Office of Aviation Medicine. The use of dry ice as pellets or powdered forms instead of the previously used block form caused concern about the relative rates of sublimation inside cargo aircraft. Dry ice shipments were believed to pose a particular hazard aboard smaller transport aircraft, where the pressurized cargo and personnel compartments are combined. Using the controlled temperature and humidity chambers of the CAMI Protection and Survival Laboratory, we performed a limited study to relate sublimation rates to dry ice from packaging, temperature, and humidity, and related them to the equation in Advisory Circular AC 103-4 for calculating the maximum allowable weight of dry ice cargo (22).

In 1983, we installed a radiant heat assembly in the combustion plenum of a 205-L chamber to allow us to thermally decompose flat materials (such as panels), using a unidirectional heat application; this would allow multilayered materials to decompose in a sequential manner such as they might in a real fire scenario. A recirculation system was developed to allow airflow around the sample, both to supply oxygen to the burning material and to prevent smoke buildup (with subsequent loss of radiant heat flux at the sample position). Using sample sizes scaled down to the 12.6-L chamber size, we compared rat response times and gas concentration/time curves in the two chambers, thus examining the feasibility for further scale-up to something nearer a real-fire situation. Beginning in October of 1983, we performed extensive toxicity tests on two aircraft seat fire-blocking materials designed to delay the involvement of thermally sensitive polyurethane foam seat cushions in an aircraft fire. Each material was decomposed by unidirectional (radiant heat) and omnidirectional (combustion tube) heat in five distinct thermal environments. Sample size was expressed on the basis of surface area per system volume to equate both the end use function of the materials and the difference in volumes of the test systems (23).

Additional material testing took up most of the Biochemistry section's activity in 1984. In March, we performed combustion tests on 4 wiring insulation samples at the request of the New York City Transit Authority. In June, we began toxicity tests on 9 panels that were concurrently being evaluated for flammability and smoke production at the FAA Technical Center using their C-133 aircraft cabin test assembly. These panels were tested using both flaming and nonflaming conditions, 12.6-L vs 265-L chambers, and unidirectional radiant heat vs omnidirectional radiant and conductive heat (combustion tube). The shortest t.s (i.e., worst case condition) occurred at the highest temperature/heat flux condition for both chambers (24). Late in 1984,

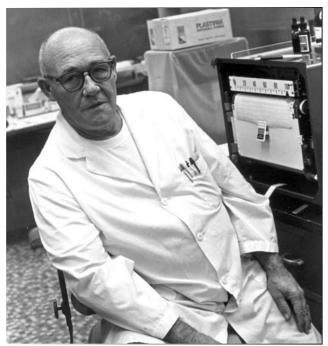
we built an additional radiant heat assembly for use with the combustion tube/small chamber unit to enable us to compare tests in the two systems using similar methods of thermal decomposition.

During this period, the FAA reviewed the possibility that passenger protective breathing devices could be designed for commercial aircraft that would provide some degree of passenger protection from smoke/combustion products and still be compatible with the decompression protective systems in current use. Dr. Crane summarized CAMI's related combustion toxicology research and its application to the problem of survival in inflight aircraft fires in a panel presentation at the 1984 Aerospace Medical Association's annual scientific sessions (25).

#### A LOOK AT INTERACTIVE EFFECTS

In 1985, we attempted to measure the changes in frequency and amplitude of respiration in the rat with increasing atmospheric carbon dioxide concentrations. With the somewhat crude equipment available, we were able to measure frequency of respiration in an unrestrained rat, but rat movement and cage motion in the rotating cage system prevented integration of the signal to obtain the actual minute respiratory volume. A rat restraining tube, designed for head-only rat exposure, was equipped with an outlet to a pressure transducer, but even the minimal animal movement within the restrainer prevented accurate integration of the respiratory volume with time. The head-only exposure insert restrainer did allow us to study the effects of CO exposures at an elevated chamber temperature (60°C) without raising the animal's core temperature and to measure the corresponding COHb levels at death. We found no statistical difference in the measured parameters between exposures at room temperature and at 60°C.

In late 1985, we acquired a commercial animal exposure chamber containing a rotating "drum" that rotated toward a shock platform; in it, a single rat was required to walk atop the drum to avoid an electrical shock. Early 1986 was spent in fitting the chamber with a flow-through system for introducing gas-air mixtures, in evaluating animal incapacitation in terms of the shock avoidance response, and in adapting a tetracyanonickelate method for the determination of gaseous HCN. These extensive preparations were directed toward a detailed reexamination of the combined effects of CO and HCN on the laboratory rat, a study interrupted some ten years earlier by the agency's material testing requirements. Exposures to CO, HCN, and to mixtures of the two gases occupied the remainder of 1986. Results indicated that the toxic potencies of the two gases were fractionally additive, with no indication of synergism. Dose-response modeling,



Abbott at the team's gas chromatograph used to measure carbon monoxide concentrations in the rat exposure chamber.

based on the concept of "fractional effective doses," was used to devise a mathematical model for estimating t<sub>i</sub> produced by defined mixtures of CO and HCN (26). Some material testing continued during this period including a fire-resistant foam produced by Polyvoltac, Canada, and some multi-layer panels manufactured by Schneller, Inc. of Kent, Ohio.

Formal requests for material testing were becoming fewer by 1987, allowing us time to plan experiments that would expand our understanding of the effects of different basic combustion parameters such as gas mixtures, heat, and changes in the pyrolysis process itself. Industry and government were beginning to understand that the ranking of materials on the basis of their potential fire toxicity was a very complex problem and that some of the early approaches to its solution had been overly simplistic. Not enough was known about the combined effects of individual combustion gases to warrant toxicity predictions from the chemical analysis of combustion products, and even with animal models, no laboratory test for fire toxicity of materials had been validated by an equivalent large-scale test model.

One of the unanswered questions involved what the quantitative effect of an irritant gas such as HCl or acrolein might be on the toxicity of the systemic toxicants, CO and HCN. In mid-1987, we began our first rat exposures to CO, acrolein, and CO-acrolein mixtures. We found evidence of an "antagonistic like" effect when acrolein was present in the CO-acrolein mixture at a concentration less toxic than that

of the CO, that is, the  $t_i$  was longer than would have been predicted for the CO concentration alone. When the toxic potency of acrolein in the mixture exceeded that of the CO,  $t_i$  began to decrease as the acrolein ceased to act simply as a respiration-depressing irritant and began to exert its own toxic effects. Regression equations were developed to predict  $t_i$  for the rat when exposed to known concentrations of CO and acrolein, singly and in mixtures (27,28).

The acquisition of a mass flow-controller allowed us to establish a dynamic flow system in an exposure chamber that allowed direct placement of an experimental animal inside the rotating cage after concentration equilibrium had been established. This eliminated the problems of exposing the rat to a changing gas concentration during initial buildup or decay and relating an average concentration to the observed response. A high flow rate through the chamber eliminated any concentration drop at animal insertion. With this modification, we examined the variation in rats' t<sub>1</sub> responses to CO at concentrations that produced nominal 5-, 10-, and 25-min t<sub>2</sub>s; corresponding relative standard deviations were 3, 10, and 19%. This enabled us to refine our CO response equation using more rigidly controlled concentration values.

Some limited material testing continued in 1987. Three panel materials proposed for use in passenger aircraft interiors were tested at the request of the Phillips 66 Company and the Boeing Commercial Airplane Company. Rankings were based on equal surface areas of the sample specimens, again in consideration for their end-use applications (29). We also tested three foam cushion materials at the request of Chestnut Ridge Foam, Inc., one of which had been evaluated as a potential seat blocking material by the FAA Technical Center. Although these tests did not represent any official acceptance or rejection of the foams (no official test criteria existed), copies of the memorandum report of our results, appropriately highlighted and labeled, were distributed by the company as promotional material at a national sales meeting (30). Certain manufacturers and users of the foams used for comparison in the study (which were not manufactured by Chestnut Ridge Foam, Inc.) were not pleased with the use of the report. That venture caused us to consider carefully any future requests for testing of manufacturer-supplied sample materials.

## SETBACKS ... AND REJUVENATED SUPPORT

In January of 1988, Dr. Charles Crane retired, having been with CAMI since its inception in 1961. His leadership of the Biochemistry Research Section, particularly after the applied research trends directed our efforts toward combustion toxicology, was characterized by a willingness to start with very basic concepts and thus lay the groundwork for the logical progression to applicable knowledge. He was a perfectionist, who believed that any analytical method accepted for use should be checked by at least one other independent method. His approach to combustion toxicology was not that of the conventional toxicologist; he insisted that animal responses be numerically equated with defined gaseous or thermal insults and that the "dose-response" relationships be mathematically modeled to make combustion toxicology a predictive rather than a purely descriptive science. In short, he brought a sense of logic and order to a research field noted for its self-serving and emotional biases.

A significant administrative crisis in the Aeromedical Research Branch led to limited funds for the entire Aviation Toxicology Laboratory in 1988; we were allotted zero equipment money and only \$800 for supplies for the year and were now reduced to two researchers, Donald Sanders and Boyd Endecott. John Abbott had previously retired in January 1986. With technical advice from CAMI's Protection and Survival Laboratory personnel, we modified an existing animal exposure chamber to provide a controlled thermal environment and a stable, flow-through CO-air atmosphere. With this equipment, we investigated the effect of moderately elevated, whole-body temperatures on the rat's t<sub>i</sub> response to fixed concentrations of CO. Equations were derived from the data to describe the t<sub>i</sub> relationships to temperature and CO concentrations, both singly and when simultaneously applied. The fractionally additive incapacitating effects reaffirmed the necessity for temperature control when the rat is used for combustion gas testing (31,32).

In 1989, we studied the relative toxic hazard rankings of identical materials by  $t_i$  and by  $LC_{50}$ , the principal indices used to measure the toxicity of combustion products. Pure polymeric standards were selected to provide uniformity of sample composition and to allow selection of a broad range of probable gas compositions; combustion conditions were identical for all tests. Relative rankings by the two endpoints were not identical. We found that delayed deaths were possible, even when incapacitation did not occur during the acute exposure and that  $LC_{50}$  values give little indication of available escape time in a fire environment. An additional determination of  $t_i$ s at the experimentally determined  $LC_{50}$  values gave a broad range of values for the same set of polymers at this defined condition of equal lethality (33).

Initial plans for 1990 research were to identify the concentrations of CO and HCN that would produce incapacitation in the laboratory rat at 5 and 35 min and to expose a sufficient number of animals to each fixed concentration to determine the variation in the t<sub>i</sub> response. This information had been requested for use by a Society of Automotive

Engineers Aviation Working Group that was involved in defining international standards for passenger protective breathing equipment and in which one of the section scientists (Donald Sanders) had previously participated. After Arvind K. Chaturvedi, Ph.D., joined the Biochemistry Research section as supervisor in January 1990, as part of a rejuvenation of support for the entire laboratory, the project was extended to include the measurements of COHb and blood cyanide at t<sub>i</sub>. Intermediate experimental results indicated the desirability of determining uptake kinetics for relating blood concentrations with chamber gas concentrations and time. Results indicated that blood concentrations were both time- and concentration-dependent and that no fixed concentration of either blood cyanide or COHb corresponded to the onset of the incapacitation response. The cyanide uptake was essentially linear, and an equation was developed to predict blood cyanide levels in the rat for known exposure times and concentrations. A limited study of rats exposed to CO-HCN mixtures indicated that any effect on individual gas uptake by the second gas in the mixture was minimal (34,35).



Chaturvedi (left) and Sanders combine efforts in setting up the team's small, flow-through combustion assembly.

## A SUMMARY OF ACCOMPLISHMENTS

Often in science, what seem to be definitive answers lead to new questions, which lead to new answers, and the cycle goes on. So what did we really accomplish in over 22 years (1970-1992)? Summarizing the preceding chronological record, we developed mathematical relationships from experimental data equating concentrations of the principal combustion gases of importance in civil aviation with  $t_i$  using the rat model. For the systemic toxicants, we demonstrated that the dose-response relationships derived from animal studies can be used to calculate dose-response relationships for humans, provided the proper scaling factors are

used. Because real fires generate multiple combustion products, we investigated the effects of simultaneous inhalation of two systemic toxicants (CO-HCN) and of a systemic toxicant paired with an irritant gas (CO-acrolein) and developed empirical equations to predict t<sub>i</sub> (in the rat) from the relative concentrations of these gases in mixtures. Finally, we quantitatively described the combined effects of elevated temperature and CO concentration on the t<sub>i</sub> response in the rat model.

In material testing studies, we investigated different methods of pyrolysis in an attempt to match pyrolysis conditions to a probable condition in a real fire environment. We noted the effects of changes in the burning conditions on the generation rate, composition, and concentration of the resulting combustion gases. Concurrently, we also investigated the specific gases produced, both by chemical analyses and by their biological effects, and compared a variety of physiological endpoints for measuring the relative toxic potencies of polymer combustion products. It became apparent that, whatever testing system was used to rank materials for combustion toxicity, materials must be compared on a quantitative basis related to their end use, i.e., foams by equal volume, panels by equal surface area, wiring insulations by equivalent length of conductor, etc. It was also apparent that all materials needed to be tested in their final formulations, including all coloring materials, fire retardants, and surface coatings, since each of these could (and frequently did) contribute to the toxicity of the resulting combustion gases.

Throughout the studies, we attempted to define each factor in the material combustion/exposure/response relationships in such a way that the information gained could be used to sequentially refine the conditions for succeeding experiments. This stepwise approach also allowed us to mathematically reevaluate data from older studies in the light of our newer findings. The in-house construction of most of the animal exposure chambers, and their subsequent operation, made us painfully aware of their original design shortcomings and allowed us to innovatively improve them to increase the precision of replication in animal exposures.

Perhaps overshadowing these contributions to combustion toxicology are advances that remain to be accomplished. Even today, state-of-the-art combustion toxicology has no generally accepted standard method for ranking materials on the basis of the relative toxicity of their combustion products. There is no "standard" fire condition, nor are there any small-scale laboratory test methods, adequately validated by comparable full-scale fire tests, that will reliably rank competing candidate materials to reflect their overall fire hazard. Regrettably, there has been little, if any, reduction in the use of rats for toxicity testing. Although we developed the products that government requested (and industry frequently resisted), there proved to be few simplistic answers to the abundance of complex problems.

## **UNFINISHED BUSINESS**

Based on our years of experimental research studies, what remains to be done before we can ever hope to meaningfully assess the potential fire hazard of materials by laboratory testing and subsequent mathematical modeling? In the area of material combustion, we must mathematically define the effects of heating rates, types of ignition and amounts of available oxygen on the rate of production, composition, and concentration of combustion products. Any laboratoryscale "test" must be validated by parallel large-scale tests that directly compare defined loads of test materials. In animal testing, it would be desirable to measure the actual uptake of the toxicants, not time-concentration measurements, and to equate these actual doses with specific physiological end points. This would enable us to make judgments on an actual dose-per-unit-weight basis, which would enhance the application of rat data to the human model. We need to examine the actual mechanisms of action for each toxicant on the living organism and its systems and to determine effects of multiple toxicants on the relative uptake of each. Fire-generated aerosols still remain a relatively unexplored problem. How are they generated and what are their biological effects? Accurate mathematical modeling will depend on the quantitative interpretation of each of these cause-effect relationships. Even if the combustion products are of an exposure that does not produce incapacitation or death, what are the long-term health risks that result?

Many of the questions related to the effects of combustion conditions and individual material screening can probably be answered by approaches utilizing a combination of engineering and bioanalytical chemistry techniques. Limited animal testing may still be required to look for the occasional "supertoxic" material that might not be detected in a screening test for expected combustion gases. We also need to remind ourselves that potential fire toxicity is only one problem in the selection of the "safest" materials for aircraft interiors. Material properties such as flammability, tensile strength, durability, cost, and amount of the specific material used, must also be considered if meaningful judgments are to be made. If the material doesn't burn, then smoke toxicity isn't a problem! What we probably should **not** do is require that material selection be regulated solely on the basis of existing, small-scale toxicity tests, which are neither sophisticated nor reliable enough to accurately evaluate acute and long-term toxic hazards for humans.

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## How to Use the Index

## Organization

The Index is organized in three sections:

- 1. Chronological Index: a cumulative list of all research reports from 1961 through 2006.
- 2. Author Index: all contributing authors, in alphabetical order.
- 3. Subject Index: subjects, listed in alphabetical order.

## Some examples are:

06-8 Williams KW: Human factors implications of unmanned aircraft accidents: Flight control problems. Above: This is an entry from the Chronological Index of research reports, shown in cumulative sequence.

Xing J -- -- 04-17, 05-4, 06-2, 06-6, 06-11, 06-15, 06-22

Above: This is an entry from the Author Index, which lists all of the research reports prepared by an author or co-author.

## Cosmic radiation

...air carrier crew, exposure of, 80-2, 92-2, 00-33, 03-16, 05-14

Above: An example of entries in the Subject Index; refers to all reports that pertain to a specific topic.

## Report Numbers

05-2 Corbett CL: Caring for precious cargo, Part II: Behavioral techniques for emergency aircraft evacuations with infants through the Type III overwing exit. ADA460057

Above: The first numbers (05-2) refer to the year and chronological number of the report. This is an abbreviated portion of the official number given each report and is found in the upper left of the report's cover page. The full report number of "05-2" is DOT/FAA/AM-05/2. The "ADA460057" is appended to the report by the National Technical Information Service. Keep the number system in mind when ordering from NTIS.

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## **Contents**

Part I	
Chronological Index	1
Part II	
Author Index4	1
Part III	
Subject Index5	1

## PART I: CHRONOLOGICAL INDEX

## 1961 Through 2006

## 1961

Trites DK: Problems in air traffic management: I. Longitudinal prediction of effectiveness of air traffic controllers. AD268954

## 1962

- 62-1 Swearingen JJ, Wheelwright CD, Garner JD: An analysis of sitting areas and pressures of man. AD271138
- 62-2 Cobb BB Jr: Problems in air traffic management: II. Prediction of success in air traffic controller school. N62-10354
- 62-3 Trites DK, Cobb BB Jr: Problems in air traffic management: III. Implications of age for training and job performance of air traffic controllers. N62-10353
- 62-4 Swearingen JJ, Mohler SR: Sonotropic effects of commercial air transport sound on birds. AD280212
- 62-5 Iampietro PF, Goldman R: Prediction of energy cost of treadmill work. AD280607
- 62-6 Balke B: Human tolerances. AD421156
- 62-7 Hasbrook AH, Earley JC: Failure of rearward-facing seat backs and resulting injuries in a survivable transport accident. AD421157
- 62-8 Smith PW: Toxic hazards in aerial application. AD421158
- 62-9 Hasbrook AH, Garner JD, Snow CC: Evacuation pattern analysis of a survivable commercial aircraft crash. AD282893
- 62-10 Daugherty JW, Lacey DE, Korty P: Problems in aerial application: I. Some biochemical effects of lindane and dieldrin on vertebrates. AD288413
- 62-11 Hawkes GR: Tactile communication. AD288414
- 62-12 Dille JR, Newton NL, Culver JF: The effects of simulated altitude on penetrating eye injuries. AD288415
- 62-13 Swearingen JJ, Hasbrook AH, Snyder R G, McFadden EB: Kinematic behavior of the human body during deceleration. AD283938
- 62-14 Swearingen JJ: Determination of centers of gravity of man. AD287156
- 62-15 Gogel WC: The visual perception of size and distance. AD287197
- 62-16 Hawkes GR: Absolute identifications of cutaneous stimuli varying in both intensity level and duration. AD295134
- 62-17 Collins WE: Manipulation of arousal and its effects on human vestibular nystagmus induced by caloric irrigation and angular accelerations. AD290348
- 62-18 Hinshaw LB, Brake CM, Iampietro PF, Emerson TE Jr: Effect of increased venous pressure on renal hemodynamics. AD295137
- 62-19 Snyder RG: A case of survival of extreme vertical impact in seated position. AD295136
- 62-20 Mohler SR: Civil aeromedical research: Responsibilities, aims, and accomplishments. AD295135
- 62-21 McFadden EB, Raeke JW, Young JW: An improved method for determining the efficiency of crew and passenger oxygen masks. AD297835

- 63-1 Emerson TE Jr, Hinshaw LB, Brake CM, Iampietro PF: The development of reversible hematuria and oliguria following elevation of renal venous pressure. AD299775
- 63-2 Mohler SR, Dille JR: Resume and index of reports of the Civil Aeromedical Research Institute, 1961-1962. AD431924
- 63-3 Collins WE: Observations on the elicitation of secondary and inverted primary nystagmus from the cat by unilateral caloric irrigation. AD413456
- 63-4 Daugherty JW, Lacey DE, Korty P: Problems in aerial application: II. Effects of chlorinated hydrocarbons on substratelinked phosphorylation. AD418504
- 63-5 Melton CE Jr: Neural control of the ciliary muscle. AD413392
- 63-6 Balke B: A simple field test for the assessment of physical fitness. AD413393

## Part I: Chronological Index

- 63-7 Tobias JV, Jeffress LA: Relation of earphone transient response to measurement of onset-duration. AD413391
- 63-8 McKenzie JM, Fowler PR, Lyne PJ: Calibration of an electronic counter and pulse height analyzer for plotting erythrocyte volume spectra. AD425598
- 63-9 Swearingen JJ, McFadden EB: Studies of air loads on man. AD602207
- 63-10 Gogel WC: The perception of depth from binocular disparity. AD429827
- 63-11 Lategola MT: In vivo measurement of total gas pressure in mammalian tissue. AD425537
- 63-12 Nagle FJ, Balke B, Ganslen RV, Davis AW: The mitigation of physical fatigue with Spartase. AD429001
- 63-13 Collins WE: Primary, secondary, and caloric nystagmus of the cat following habituation to rotation. AD428756
- 63-14 Collins WE: Nystagmus responses of the cat to rotation and to directionally equivalent and nonequivalent stimuli after unilateral caloric habituation. AD425565
- 63-15 Snyder RG: Human survivability of extreme impacts in free-fall. AD425412
- 63-16 Emerson TE Jr, Brake CM, Hinshaw LB: Mechanisms of action of the insecticide endrin. AD431299
- 63-17 Tobias JV: Application of a "relative" procedure to a problem in binaural beat perception. AD428899
- 63-18 Balke B: Experimental evaluation of work capacity as related to chronological and physiological aging. AD431301
- 63-19 Wernick JS, Tobias JV: A central factor in pure tone auditory fatigue. AD428737
- 63-20 Gogel WC: The visual perception of spatial extent. AD432587
- 63-21 Tang PC, Dille JR: In-flight loss of consciousness: A case report. AD430394
- 63-22 Hinshaw LB, Page BB, Brake CM, Emerson TE Jr, Masucci FD: The mechanisms of intrarenal hemodynamic changes following acute arterial occlusion. AD431302
- 63-23 Higgins EA, Iampietro PF, Adams T, Holmes DD: The effects of a tranquilizer on body temperature. AD432484
- 63-24 Dille JR, Smith PW: Central nervous system effects of chronic exposure to organophosphate insecticides. AD434090
- 63-25 Adams T, Funkhouser GE, Kendall WW: A method for the measurement of physiologic evaporative water loss. AD603418
- 63-26 Reins DA, Holmes DD, Hinshaw LB: Acute and chronic effects of the insecticide endrin on renal function and renal hemodynamics. AD602206
- 63-27 Dille JR, Crane CR, Pendergrass GE: The flammability of lip, face, and hair preparations in the presence of 100% oxygen. AD602204
- 63-28 Gogel WC: Size cues and the adjacency principle. AD602205
- 63-29 Collins WE: Task-control of arousal and the effects of repeated unidirectional angular acceleration on human vestibular responses. AD603419
- 63-30 Snyder RG, Ice J, Duncan JC, Hyde AS, Leverett S Jr: Biomedical research studies in acceleration. AD601531 Supplement-AD801793
- 63-31 Trites DK, Cobb BB Jr: Problems in air traffic management: IV. Comparison of preemployment, job-related experience with aptitude tests as predictors of training and job performance of air traffic control specialists. AD603416
- 63-32 Hinshaw LB, Emerson TE Jr, Brake CM: Mechanism of autoregulation in the intact kidney. AD603417
- 63-33 Dill DB, Robinson S, Balke B, Newton JL: Work tolerance: Age and altitude. AD603932
- 63-34 Ganslen RV, Balke B, Phillips EE, Nagle F: Effects of some tranquilizing, analeptic, and vasodilating drugs on physical work capacity and orthostatic tolerance. AD603930
- 63-35 Pearson RG: Human factors aspects of lightplane safety. AD603931
- Tech. Pub. #1 Collins WE, Tobias JV, Capps MJ, Allen ME: Annotated bibliography of recently translated material. I. AD424640

- Wentz AE: Studies on aging in aviation personnel. AD456652
- Naughton J, Balke B, Nagle F: The effect of physical conditioning on an individual before and after suffering a myocardial infarction. AD456653

- Nagle FJ, Balke M: The gradational step test for assessing cardiorespiratory capacity: An experimental evaluation of tread-mill and step test procedures. AD456654
- 64-4 Spieth W: Cardiovascular health status, age, and psychological performance. AD453578
- 64-5 Moser KM: Current status of clot dissolution therapy. AD453579
- 64-6 Seipel JH, Wentz AE: Unsuspected neurologic disease in aviation personnel: Survival following seizures in flight. AD453580
- 64-7 Houk VN, Hufnagel CA, McClenathan JE, Moser KM: Chronic thrombotic obstruction of major pulmonary arteries. AD453581
- 64-8 Moser KM, Perry RB, Luchsinger PC: Cardiopulmonary consequences of pyrogen-induced hyperpyrexia in man.
- 64-9 Freud SL: Duration of spiral aftereffect as a function of retinal size, retinal place, and hemiretinal transfer. AD618588
- 64-10 Freud SL: Duration as a measure of the spiral aftereffect. AD618589
- 64-11 Pinkerson AL, Kot PA, Knowlan DM: Effect of glyceryl trinitrate on pulmonary vasculature of anesthetized dogs. 64-12 Scarborough WR: Comments on progress in ballistocardiographic research and the current state of the art. AD455651
- 64-13 Gogel WC: The size cue to visually perceived distance. AD456655
- 64-14 Capps MJ, Collins WE: Effects of bilateral caloric habituation on nystagmus responses of the cat. AD455652
- 64-15 Collins WE, Huffman HW: Design and performance characteristics of a mechanically driven vestibular stimulator. AD456656
- 64-16 Tobias JV, Collins WE, Allen ME: Aviation medicine translations: Annotated bibliography of recently translated material. II. AD456670
- 64-17 Freud SL: The physiological locus of the spiral aftereffect. AD611881
- 64-18 Melton CE Jr: Physiological recordings from pilots operating an aircraft simulator. AD456671
- 64-19 Perloff JK: The recognition of strictly posterior myocardial infarction by conventional scalar electrocardiography. AD611882
- 64-20 FAA Aviation Medical Library: Aviation medical papers and reports: a bibliography. AD613364

- 65-1 Capps MJ, Collins WE: Auditory fatigue: Influence of mental factors. AD459636
- 65-2 Collins WE, Capps MJ: Effects of several mental tasks on auditory fatigue. AD459637
- 65-3 Reighard, HL: Medical services at airports. AD611883
- 65-4 Seipel JH, Ziemnowicz SAR, O'Doherty DS: Cranial impedance plethysmography-Rheoencephalography as a method of detection of cerebrovascular disease. AD611884
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- 65-19 Cobb BB Jr: Problems in air traffic management: V. Identification and potential of aptitude test measures for selection of tower air traffic controller trainees. AD620722
- 65-20 Swearingen JJ: Tolerances of the human face to crash impact. AD621434
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- 65-25 Feinberg R, Podolak E: Latency of pupillary reflex to light stimulation and its relationship to aging. AD689809
- 65-26 Snow CC, Snyder RG: Anthropometry of air traffic control trainees. N66-25185
- 65-27 Brake CM, Reins D, Wittmers LE, Hinshaw LB: Intrarenal hemodynamic changes following acute partial renal arterial occlusion. AD649263
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- 66-18 Swearingen JJ: Evaluation of head and face injury potential of current airline seats during crash decelerations. AD653869
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- 66-38 Mertens HW: A homogeneous field for light adaptation.
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- 66-40 Swearingen JJ: Evaluation of various padding materials for crash protection. AD647048
- 66-41 McKenzie JM, Fiorica V: Physiological responses of pilots to severe-weather flying. AD646871
- 66-42 Garner JD, Blethrow JG: Emergency evacuation tests of a crashed L-1649. AD645423

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- 67-11 Seipel JH: The biophysical basis and clinical applications of rheoencephalography. AD673082
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- 67-13 Young JW: A functional comparison of basic restraint systems. AD660202
- 67-14 Swearingen JJ: An evaluation of potential decompression hazards in small pressurized aircraft. AD660203
- 67-15 Melton CE Jr, Wicks SM: In-flight physiological monitoring of student pilots. AD665660
- 67-16 Lewis MF: Cross-modality matching of loudness to brightness for flashes of varying luminance and duration. AD664463
- 67-17 Funkhouser GE, Billings SM: A portable device for the measurement of evaporative water loss. AD664465
- 67-18 Gogel WC: Cue-enhancement as a function of task-set. AD664466
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- 67-23 Veregge EJ: Type airman certification as related to accidents. AD663688
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- 68-7 Allen ME, Mertens RA: Aviation medicine translations: Annotated bibliography of recently translated material. V. AD673665
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- 68-18 Higgins EA, Davis AW Jr, Vaughan JA, Funkhouser GE, Galerston EM: The effects of alcohol at three simulated aircraft cabin conditions. AD686671
- 68-19 Snyder RG, Snow CC: Fatal injuries resulting from extreme water impact. AD688424
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- 68-21 Tobias JV: Cockpit noise intensity: Fifteen single-engine light aircraft. AD686425
- 68-22 Hasbrook AH: A comparison of effects of peripheral vision cues on pilot performance during instrument flight in dissimilar aircraft simulators. AD688425
- 68-23 Fiorica V: A table for converting pH to hydrogen ion concentration [H+] over the range 5-9. AD688120
- 68-24 Snyder RG, Snow CC, Crosby WM, Hanson P, Fineg J, Chandler R: Impact injury to the pregnant female and fetus in lap belt restraint. AD689359
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- 69-7 Pearson DW, Thackray RI: Consistency of performance change and autonomic response as a function of expressed attitude toward a specific stress situation. AD697944
- 69-8 Thackray RI: Patterns of physiological activity accompanying performance on a perceptual-motor task. AD697945
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- 69-13 Snyder RG, Snow CC, Young JW, Price GT, Hanson PG: Experimental comparison of trauma in lateral (+Gy), rearward-facing (+Gx), and forward-facing (-Gx) body orientations when restrained by lap belt only. AD707185
- 69-14 Chiles WD, Jennings AE: Effects of alcohol on complex performance. AD703633
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- 69-17 Siegel PV, Gerathewohl SJ, Mohler SR: Time-zone effects on the long-distance air traveler. AD702443
- 69-18 Siegel PV, Mohler SR, Cierebiej A: The safety significance of aircraft accident post mortem findings. AD704473
- 69-19 Pearson DW, Clark G, Moore CM: A comparison of the behavioral effects of various levels of chronic disulfoton poisoning. AD704470
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- 69-21 Thackray RI, Touchstone RM: Recovery of motor performance following startle. AD704472
- 69-22 Swearingen JJ, Badgley JM, Braden GE, Wallace TF: Determination of centers of gravity of infants. AD708514
- 69-23 Brecher MH, Brecher GA: Motor effects from visually induced disorientation in man. AD708425
- 69-24 Gerathewohl SJ: Fidelity of simulation and transfer of training: A review of the problem. AD706744

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- 70-5 Higgins EA, Vaughan JA, Funkhouser GE: Blood alcohol concentrations as affected by combinations of alcoholic beverage dosages and altitudes. AD709328
- 70-6 Tobias JV: Auditory processing for speech intelligibility improvement. AD717394
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- 70-9 Gerathewohl SJ, Morris Everett W, Sirkis JA: Anti-collision lights for the supersonic transport (SST). AD713488
- 70-10 Collins WE, Schroeder DJ, Rice N, Mertens RA, Kranz G: Some characteristics of optokinetic eye-movement patterns: A comparative study. AD715440
- 70-11 Revzin AM: Some acute and chronic effects of endrin on the brain. AD715452
- 70-12 Mohler SR: Physiologically tolerable decompression profiles for supersonic transport type certification. AD713055
- 70-13 Crane CR, Sanders DC, Abbott JK: A comparison of three serum cholinesterase methods. AD715439
- 70-14 Karson S, O'Dell JW: Performance ratings and personality factors in radar controllers. AD715247
- 70-15 Lewis MF, Mertens, HW: Two-flash thresholds as a function of comparison stimulus duration. AD716645
- 70-16 Snow CC, Carroll JJ, Allgood MA: Survival in emergency escape from passenger aircraft. AD735388
- 70-17 Collins WE: Effective approaches to disorientation familiarization for aviation personnel. AD719003

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- 70-20 McFadden EB, Smith RC: Protective smoke hood studies. AD727021
- 70-21 Lategola MT, Harrison HF: A device and method for rapid indirect measurement of human systolic and diastolic blood pressures. AD722032
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- 71-2 Melton CE Jr, McKenzie JM, Polis BD, Funkhouser GE, Iampietro PF: Physiological responses in air traffic control personnel: O'Hare Tower. AD723465
- 71-3 Swearingen JJ: General aviation structures directly responsible for trauma in crash decelerations. AD728728
- 71-4 Iampietro PF: Use of skin temperature to predict tolerance to thermal environments. AD723466
- 71-5 Mertens RA, Goulden DR, Lacy CD, Jones KN: Aviation medicine translations: Annotated bibliography of recently translated material. VI. AD723467
- 71-6 Schroeder DJ: Alcohol and disorientation-related responses. I. Nystagmus and "vertigo" during caloric and optokinetic stimulation. AD728314
- 71-7 Thackray RI, Jones KN: Effects of conflicting auditory stimuli on color-word interference and arousal. AD727018
- 71-8 Lategola MT: Biodynamic evaluation of air traffic control students between 1960-1963. AD726254
- 71-9 Cierebiej A, Mohler SR, Stedman VG: Physician pilot- in-command flight accidents, 1964 through 1970. AD724286
- 71-10 Gerathewohl SJ, Mohler SR, Siegel PV: Medical and psychological aspects of mass air transportation. AD726286
- 71-11 Fiorica V, Burr MJ, Moses R: Effects of low-grade hypoxia on performance in a vigilance situation. AD727019
- 71-12 Swearingen JJ: Acceptance tests of various upper torso restraints. AD726253
- 71-13 Swearingen JJ: Tolerances of the human brain to concussion. AD726287
- 71-14 Smith RC: Assessment of a "stress" response-set in the Composite Mood Adjective Check List. AD727020
- 71-15 Fiorica V, Moses R: Automated differential fluorometric analysis of norepinephrine and epinephrine in blood plasma and urine. AD729535
- 71-16 Schroeder DJ: Alcohol and disorientation-related responses. II. Nystagmus and "vertigo" during angular acceleration. AD730629
- 71-17 Chiles WD, Iampietro PF, Higgins EA, Vaughan JA, West G, Funkhouser GE: Combined effects of altitude and high temperature on complex performance. AD729536
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- 71-19 Lategola MT: Changes in cardiovascular health parameters over an eight-year interval in an ATC population segment. AD729537
- 71-20 Collins WE, Gilson RD, Schroeder DJ, Guedry FE Jr: Alcohol and disorientation-related responses. III. Effects of alcohol ingestion on tracking performance during angular acceleration. AD728843
- 71-21 Smith RC, Melton CE Jr, McKenzie JM: Affect adjective check list assessment of mood variations in air traffic controllers. AD729832
- 71-22 Brecher MH, Brecher GA: Effect of a moving optical environment on the subjective median. AD728316
- 71-23 Melton CE Jr, Fiorica V: Physiological responses of low-time private pilots to cross-country flying, AD728317
- 71-24 Hasbrook AH, Rasmussen PG: Aural glide slope cues: Their effect on pilot performance during in-flight simulated ILS instrument approaches, AD731848
- 71-25 Norwood GK: The philosophy and limitations of FAA aeromedical standards, policies, and procedures. AD729538
- 71-26 Friedberg W, Nelson JM: Calibration of the Concorde radiation detection instrument and measurements at SST altitude. AD732789

- 71-27 Lewis MF, Steen JA: Color-defective vision and the recognition of aviation color signal light flashes. AD729539
- 71-28 Chiles WD, Smith RC: A nonverbal technique for the assessment of general intellectual ability in selection of aviation personnel. AD728844
- 71-29 Thackray RI, Touchstone RM, Jones KN: The effects of simulated sonic booms on tracking performance and autonomic response. AD729833
- 71-30 Smith RC, Cobb BB Jr, Collins WE: Attitudes and motivational factors in terminal area air traffic control work. AD730630
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- 71-35 Smith RC: Personality assessment in aviation: An analysis of the item ambiguity characteristics of the 16PF and MMPI. AD736266
- 71-36 Cobb BB Jr, Lay CD, Bourdet NM: The relationship between chronological age and aptitude test measures of advanced-level air traffic control trainees. AD733830
- 71-37 McFadden EB, Young JW: Evaluation of an improved flotation device for infants and small children. AD729836
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- 71-39 Hill RJ, Collins WE, Schroeder DJ: Alcohol and disorientation-related responses: V. The influence of alcohol on positional, rotatory, and coriolis vestibular responses over 32-hour periods. AD735389
- 71-40 Cobb BB Jr: Air traffic aptitude test measures of military and FAA controller trainees. AD737871
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- 72-3 Sirkis JA: The benefits of the use of shoulder harness in general aviation aircraft. AD739943
- 72-4 Billings CE, Wick RL Jr, Gerke RJ, Chase RC: The effects of alcohol on pilot performance during instrument flight. AD740778
- 72-5 Chiles WD, Jennings AE, West G: Multiple-task performance as a predictor of the potential of air traffic controller trainees. AD741736
- 72-6 Lowrey DL, Langston ED, Reed W, Swearingen JJ: Effectiveness of restraint equipment in enclosed areas. AD739944
- 72-7 Langston ED, Swearingen JJ: Evaluation of a fiberglass instrument glare shield for protection against head injury. AD740732
- 72-8 Zeiner AR, Brecher GA: Effects of backscatter of brief high-intensity light on physiological responses of instrument-rated pilots and non-pilots. AD744234
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- 72-12 Crane CR, Sanders DC, Abbott JK: A comparison of serum cholinesterase methods: II. AD744866

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- 72-15 Swearingen JJ, Wallace TF, Blethrow JG, Rowlan DE: Crash survival analysis of 16 agricultural aircraft accidents. AD745257
- 72-16 Jones KN, Goulden DR, Grimm EJ: Aviation medicine translations: Annotated bibliography of recently translated material. VII. AD747125
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- 72-22 Cobb BB Jr, Mathews JJ, Lay CD: A comparative study of female and male air traffic controller trainees. AD751312
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#### 1987

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- 02-22 Moertl PM, Canning JM, Gronlund SD, Dougherty MRP, Johansson J, Mills SH: Aiding planning in air traffic control: An experimental investigation of the effects of perceptual information integration. ADA409992
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- O3-3 Taylor HL, Talleur DA, Bradshaw GL, Eanuel TW Jr., Rantanen E, Hulin CL, Lendrum L: Effectiveness of personal computers to meet recency of experience requirements. ADA413334
- O3-4 Shappell SA Wiegmann DA: A human error analysis of general aviation controlled flight into terrain accidents occurring between 1990-1998. ADA417230
- 03-5 Uhlarik J, Comerford DA: Information requirements for traffic awareness in a free-flight environment: An application of the FAIT Analysis. ADA413832
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- O3-7 Akin A, Chaturvedi AK: Prevalence of selective serotonin reuptake inhibitors in pilot fatalities of civil aviation accidents, 1990-2001. ADA423836
- 03-8 Pfleiderer EM: Development of an empirically based index of aircraft mix. ADA417231
- 03-9 Gowdy V, DeWeese R: Human factors associated with the certification of airplane passenger seats: Life preserver retrieval. ADA417209
- 03-10 Hackworth CA, Peterson LM, Jack DG, Williams CA, Hodges BE: Examining hypoxia: A survey of pilots' experiences and perspectives on altitude training. ADA417131
- 03-11 Hackworth CA, King SJ, Detwiler CA: The employee attitude survey 2000: Perspectives on its process and utility. ADA417166
- 03-12 Nakagawara VB, Montgomery RW, Dillard A, McLin L, Connor CW: Effects of laser illumination on operational and visual performance of pilots conducting terminal operations. ADA423865

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- 03-14 Dollar C, Broach D, Schroeder D: Personality characteristics of air traffic control specialists as predictors of disability retirement. ADA424266
- 03-15 Corbett CL, McLean GA, Whinnery JE: Access-to-Egress II: Subject management and injuries in a study of emergency evacuation through the Type-III exit. ADA423728
- 03-16 Friedberg W, Copeland K: What aircrews should know about their occupational exposure to ionizing radiation. ADA423589
- 03-17 Williams K, Ball J: Usability and effectiveness of advanced general aviation cockpit displays for instrument flight procedures. ADA423591
- 03-18 Johnson RD, Lewis RJ, Canfield DV, Blank, CL: Ethanol origin in postmortem urine: An LC/MS determination of serotonin metabolites. ADA423727
- 03-19 Pounds J, Ferrante A: FAA strategies for identifying and reducing operational error causal factors. ADA423665
- 03-20 King RE, Retzlaff PD, Detwiler C, Schroeder DJ, Broach D: Use of personality assessment measures in the selection of air traffic control specialists. ADA423269
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- 03-23 Lewis RJ, Johnson RD, Angier MK, Ritter RM, Drilling HS, Williams SD: Analysis of cocaine, its metabolites, prolysis products, and ethanol adducts in postmortem fluids and tissues using Zymark automated solid-phase extractions and gas chromatography-mass spectrometry. ADA423349
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- O4-3 Garner RP, Ultrecht JS: Performance criteria for development of extended use protective breathing equipment. ADA423233
- 04-4 Johnson RD, Lewis RJ, Angier MK, Vu NT: The formation of ethanol in postmortem tissues. ADA423300
- 04-5 Beringer DB, Ball JD: The effects of NEXRAD graphical data resolution and direct weather viewing on pilot's judgments of weather severity and their willingness to continue a flight. ADA423239
- 04-6 Nakagawara VB, Montgomery RW, Wood KJ: Demographics and vision restrictions in civilian pilots: Clinical implications. ADA423237
- 04-7 Garner RP, Wong KL, Ericson SC, Baker AJ, Orzechowski JA: CFD validation for contaminant transport in aircraft cabin ventilation flow fields. ADA423999
- 04-8 Broach D: Methodological issues in the study of airplane accident rates by pilot age: Effects of accident and pilot inclusion criteria and analytic strategy. ADA423237
- 04-9 Nakagawara VB, Montgomery RW, Dillard AE, McLin LN, Connor CW: The effects of laser illumination on operational and visual performance of pilots during final approach. ADA425392
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- 04-12 McLean GA, Palmerton DA, Corbett CL, Larcher KG, McDown JR: Simulated evacuations into water. ADA427908
- 04-13 Johnson RD, Lewis RJ, Canfield DV, Dubowski KM, Blank CL: Accurate assignment of ethanol origin in postmortem urine: A case study. ADA427914
- 04-14 Milburn NJ, Mertens HW: Predictive validity of the aviation lights test for testing pilots with color vision deficiencies. ADA428358
- 04-15 Angier MK, Lewis RJ, Chaturvedi AK, Canfield DV: Gas chromatographic/mass spectrometric differentiation of atenolol, metoprolol, propanolol, and an interfering metabolite product of metoprolol. ADA428964
- 04-16 DeJohn CA, Wolbrink AM, Larcher JG: In-flight medical incapacitation and impairment of U.S. airline pilots: 1993 to 1998. ADA428688
- 04-17 Xing J: Measures of information complexity and the implications for automation design. ADA428690
- 04-18 DeWeese R, Moorcroft D: Evaluation of a head injury criteria component test device. ADA428692
- 04-19 McLean GA, Cosper DK: Availability of passenger safety information for improved survival in aircraft accidents. ADA372580
- 04-20 Williams KW, Ball JD: Usability and effectiveness of advanced general aviation cockpit displays for visual flight procedures. ADA423591
- 04-21 Dollar CS, Schroeder DJ: A longitudinal study of Myers-Briggs personality types in air traffic controllers. ADA460091
- 04-22 Hackworth CA, Cruz CE, Goldman S, Jack DG, King SJ, Twohig P: Employee attitudes within the Federal Aviation Administration. ADA460092
- 04-23 Hackworth CA, Cruz CE, Jack DG, Goldman S, King SJ: Employee attitudes within the air traffic organization. ADA460936
- 04-24 Williams K: A summary of unmanned aircraft accident/incident data: Human factors implications. ADA460102

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- O5-3 Collins WE, Wade KJ: A milestone of aeromedical research contributions to civil aviation safety: The 1000th report in the CARI/OAM series. ADA460106
- 05-4 Xing J, Manning CA: Complexity and automation displays of air traffic control: Literature review and analysis. ADA460107
- 05-5 Bailey L, Schroeder DJ, Pounds J: The Air Traffic Control Operational Errors Severity Index: An initial evaluation. ADA460573
- 05-6 Broach D: Review of the scientific basis for the mandatory separation of an ATCS at Age 56. ADA460056
- 05-7 Knecht WR, Harris H, Shappell S: The influence of visibility, cloud ceiling, financial incentive, and personality factors on general aviation pilots' willingness to take off into marginal weather: Part I. The data and preliminary conclusions. ADA460734
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- 05-9 Canfield DV, Chaturvedi AK, Dubowski KM: Interpretation of carboxyhemoglobin and cyanide concentrations in relation to aviation accidents. ADA460835
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- 05-11 Johnson RD, Lewis RJ, Hattrup RA: Poppy seed consumption or opiate use: The determination of thebaine and opiates of abuse in postmortem fluids and tissues. ADA460858

- 05-12 Beringer DB, Harris HC Jr: A comparison of baseline hearing thresholds between pilots and non-pilots and the effects of engine noise. ADA460838
- 05-13 King SJ, Cruz CE, Jack DG, Thomas S, Hackworth CA: 2003 Employee Attitude Survey: Analysis of employee comments. ADA460830
- 05-14 Copeland K, Sauer HH, Friedberg W: Solar radiation alert system. ADA460733
- 05-15 Knecht WR: Pilot willingness to take off into marginal weather, Part II: antecedent overfitting with forward stepwise logistic regression. ADA460841
- 05-16 Pfleiderer EM: Relationship of the aircraft mix index with performance and objective workload evaluation research measures and controllers' subjective complexity ratings. ADA460790
- 05-17 Palmerton D: Fatality and injury rates for two types of rotorcraft accidents. ADA460769
- 05-18 Garner RP, Mandella JG Jr: Reliability of the gas supply in the air force emergency passenger oxygen system. ADA460831
- 05-19 Prinzo OV: Terminal radar approach control: Measures of voice communications system performance. ADA460833
- 05-20 Chaturvedi AK, Craft KJ, Canfield DV, Whinnery JE: Epidemiology of toxicological factors in civil aviation accident pilot fatalities, 1999-2003. ADA460798
- 05-21 Nakagawara VB, Montgomery RW, Good GW: Medical surveillance programs for aircraft maintenance personnel performing nondestructive inspection and testing. ADA460862
- 05-22 Broach D, Schroeder D: Relationship of air traffic control specialist age to en route operational errors. ADA460816
- 05-23 Beringer DB, Ball JD, Brennan K, Taite S: Comparison of a typical electronic attitude-direction indicator with terraindepicting primary flight displays for performing recoveries from unknown attitudes: Using difference and equivalence tests. ADA460873
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- 05-25 Scarborough A, Bailey LL, Pounds J: Examining ATC operational errors using the Human Factors Analysis and Classification System. ADA460879

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- 06-4 Goldman SM, Manning C, Pfleiderer E: Static sector characteristics and operational errors. ADA460882
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- O6-6 Xing J, Schroeder DJ: Reexamination of color vision standards, Part II. A computational method to assess the effect of color deficiencies in using ATC displays. ADA463063
- 06-7 Detwiler C, Hackworth C, Holcomb K, Boquet A, Pfleiderer E, Wiegmann D, Shappell, S: Beneath the tip of the iceberg: A human factors analysis of general aviation accidents in Alaska vs. the rest of the United States. ADA460891
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- 06-13 Nesthus TE, Cruz C, Hackworth C, Boquet A: An assessment of commuting risk factors for air traffic control specialists. ADA460857
- 06-14 Kupfer DM, Huggins M, Cassidy B, Vu N, Burian D, Canfield D: A rapid and inexpensive PCR-based STR genotyping method for identifying forensic specimens. ADA460885
- 06-15 Xing J: Color and visual factors in ATC displays. ADA460886
- 06-16 Dattel AR, King RE: Reweighing AT-SAT to mitigate group score differences. ADA461242
- 06-17 Johnson RD, Lewis RJ, Angier MK: The LC/MS quantitation of Vardenafil (Levitra®) in postmortem biological specimens. ADA460865
- 06-18 Shappell SA, Detwiler CA, Holcomb KA, Hackworth CA, Boquet AJ, Wiegmann DA: Human error and commercial aviation accidents: A comprehensive, fine-grained analysis using HFACS. ADA463865
- 06-19 Caldwell DC, Lewis RJ, Shaffstall RM, Johnson RD: Sublimation rate of dry ice packaged in commonly used quantities by the air cargo industry. ADA461451
- 06-20 Pounds J, Rodgers MD, Thompson D, Jack DG: Developing temporal markers to profile operational errors. ADA461407
- 06-21 Schroeder D, Bailey L, Pounds J, Manning C: A human factors review of the operational error literature. ADA461408
- 06-22 Xing J: Color analysis in air traffic control displays, Part I. Radar displays. ADA461409
- 06-23 Nakagawara VB, Wood KJ, Montgomery RW: A review of recent laser illumination events in the aviation environment. ADA461728
- 06-24 Shappell S, Wiegmann D: Developing a methodology for assessing safety programs targeting human error in aviation. ADA461400
- 06-25 Prinzo OV, Hendrix AM, Hendrix R: The outcome of ATC message complexity on pilot readback performance. ADA461355
- 06-26 Milburn NJ, Dobbins L, Pounds J, Goldman S: Mining for information in accident data. ADA464086
- 06-27 Baker AJ, Ericson SC, Orzechowski JA, Wong KL, Garner RP: Validation for CFD prediction of mass transport in an aircraft passenger cabin. ADA465914
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- 06/29 Manning CM, Pfleiderer EM: Relationship of sector activity and sector complexity to air traffic controller taskload. ADA463881
- 06/30 Dollar C, Broach D: Comparison of intent-to-leave with actual turnover within the FAA. ADA463866

## PART II: AUTHOR INDEX

Author Report Number Author Report Number Baxter NE----- 84-6, 90-1 Abbott JK ----- 70-4, 70-13, 72-12, 77-9, 83-12, 85-4, 86-3, 86-5 Bedell RHS ----- 67-22 Adams HJ ----- 98-5 Behn LD ----- 97-12, 99-19, 00-3 Adams T-----63-23, 63-25, 65-16, 65-28, 65-29, 65-30, Beiergrohslein D-78-26 66-23 Bergey KH ----- 72-27 Agee FL Jr----- 66-24 Bergin JM----- 73-5 Agen RA----- 98-8, 02-24 Beringer DB ----- 96-15, 96-16, 97-24, 00-26, 02-7, 02-19, Agnew BO ----- 00-12, 02-24 04-5, 05-12, 05-23 Akin A ----- 03-7 Berkley WJ----- 65-5, 65-6 Albright CA----- 96-5, 98-26 Berninger D ----- 91-16 Allen ME----- TechPub#1, 64-16, 65-17, 66-1, 66-2, 68-7 Besco RO ----- 95-5 Allgood MA ----- 70-16, 75-2, 75-13 Billings CE----- 72-4 Alluisi EA ---- 78-34 Billings SM ----- 67-17 Anderson JA ----- 79-23, 80-12 Birkey M ----- 95-28 Angier MK----- 03-23, 04-4, 04-15, 06-17 Biron WJ ----- 84-1 Antuñano MJ----- 93-3, 01-15, 06-1, 06-1 Bishop J ----- 06-10 Armenia-Cope R-93-14 Blanchard RE---- 93-9, 94-5, 95-6 Armstrong R----- 66-17 Blank CL----- 00-20, 03-18, 04-13 Arnell F----- 97-22 Bleckley MK----- 97-22 Ashby FK ----- 67-8 Blethrow JG ----- 66-42, 70-19, 72-15, 77-11, 78-3, 79-22, 80-12 Atocknie PA ----- 89-10 Aul JC ----- 92-5 Blossom CW ---- 78-31 Bolding FA----- 80-8 Aviation Medical Library FAA ----- 64-20 Bone RS----- 03-2 Boone JO ---- 78-10, 78-36, 79-14, 79-21, 80-5, 80-7, R 80-15, 82-2, 82-11, 82-18, 83-6, 83-9 Booze CF Jr----- 68-5, 68-9, 69-11, 70-18, 72-13, 73-8, Badgley JM ----- 69-22 73-10, 74-5, 75-5, 76-7, 77-10, 77-20, 78-21, 79-19, 80-8, 81-9, 81-14, 83-18, Bailey JP-----73-16, 74-9, 75-8, 77-18, 78-11 84-3, 84-8, 85-6, 87-7, 89-2, 90-7 Bailey LL ----- 96-24, 98-24, 99-17, 99-24, 99-25, 99-27, Boquet A ----- 02-8, 02-13, 02-20, 05-24, 06-7, 06-13, 00-14, 00-17, 00-25, 00-28, 01-19, 01-20, 06-18 02-18, 06-21, 05-5, 05-25 Boren HK----- 00-22 Bain DL ----- 97-22 Bourdet NM----- 71-36 Baisden DL ---- 06-1 Boyer D ----- 94-17, 94-26, 95-23, 96-9 Baker AJ ----- 04-7, 06-27 Braden GE ----- 69-22, 73-1 Baker SP----- 96-3 Bradshaw GL ---- 03-3 Balke B ----- 62-6, 63-6, 63-12, 63-18, 63-33, 63-34, 64-2, 64-3, 66-36 Brake CM----- 62-18, 63-1, 63-16, 63-22, 63-32, 65-27 Ball JD-----03-17, 04-5, 04-20, 05-23 Branson DM ----- 85-11 Bannister JR ---- 78-4 Brecher GA ----- 69-23, 70-2, 71-22, 72-8 Barile AB ----- 96-5 Brecher MH ----- 69-23, 70-2, 71-22 Barnard C----- 66-16 Brecht-Clark J ---- 94-4 Bartanowicz RS -- 86-2 Brennan R ----- 05-23 Battisie V----- 03-2 Britton TW ----- 93-20, 95-15

Author	Report Number	Author	Report Number
Broach DM	91-4, 91-11, 91-18, 92-26, 93-4, 94-4, 94-9, 96-6, 96-13, 97-4, 97-15, 97-19, 98-8, 98-22, 98-23, 99-16, 99-24, 00-15, 02-9, 03-14, 03-20, 04-8, 05-6, 05-22, 06-30	Collins WE	62-17, 63-3, 63-13, 63-14, 63-29, Tech. Pub.#1, 64-14, 64-15, 64-16, 65-1, 65-2, 65-17, 65-18, 65-24, 66-37, 67-2, 67-6, 67-7, 67-12, 67-19, 68-2, 68-10, 68-28,
Broadhurst JL	72-30		69-15, 69-20, 70-10, 70-17, 71-20, 71-30,
Bruni CB	69-6, 69-16		71-31, 71-34, 71-39, 72-34, 72-35, 73-17, 73-18, 74-2, 74-3, 74-7, 75-1, 75-3, 75-4,
Bryant KD			76-12, 76-14, 77-24, 78-13, 79-7, 79-9,
Burian D			79-26, 80-7, 81-15, 81-16, 82-19, 83-6, 84-6,
Busby DE	77-11 <b>C</b>		85-3, 85-5, 86-9, 87-4, 88-2, 88-3, 89-7, 90-1, 90-4, 91-8, 92-1, 93-2, 94-1, 95-1, 95-3, 95-7, 95-13, 96-1, 96-21, 96-22, 97-1, 98-1, 99-1, 00-1, 01-1, 03-1, 05-1, 05-3
Caldwell DC	06-19	Coltman JW	83-3
Caldwell L		Comerford DA	02-3, 03-5
Cameron-Landis		Comperatore C	00-10
	91-12, 92-23, 92-24, 92-25, 94-14, 94-16,	Connor CW	03-12, 04-9
Carmera D v	95-26, 95-28, 96-14, 96-17, 98-5, 98-18,	Constant GN	73-19, 76-4
	98-21, 99-14, 99-15, 99-29, 00-9, 00-16,	Convey JJ	83-11, 85-7, 86-6
	00-21, 00-22, 00-29, 00-34, 01-12, 02-14, 02-15, 03-18, 03-22, 03-24, 04-1, 04-13,	Cook EA	72-30, 78-23
	04-15, 05-8, 05-9, 05-20, 06-12, 06-14	Copeland K	00-5, 03-16, 05-14
Canning IM	01-16, 02-1, 02-22	Corbett CL	01-18, 02-16, 03-15, 04-2, 04-12, 05-2
	Tech.Pub.#1, 64-14, 65-1, 65-2	Cosper DK	98-1, 04-19
	00-29, 03-22, 03-24	Court MC	97-20
Carroll JJ		Craft KJ	05-20
Cassidy B		Crain RA	65-17, 66-2
Chandler RF	68-24, 72-27, 74-4, 76-9, 77-11, 78-6, 78-12, 78-23, 78-24, 79-17, 80-12, 82-8, 83-16	Crane CR	63-27, 67-21, 70-4, 70-13, 72-12, 77-9, 78-26, 83-12, 85-4, 86-1, 86-3, 86-5, 86-8, 89-4, 90-15
Chase RC		Cremer RL	
Chaturvedi AK	91-17, 93-7, 93-8, 94-7, 94-18, 95-8, 95-26, 97-14, 98-10, 98-18, 98-21, 99-11,		68-6, 68-24, 69-3, 69-5
	99-14, 99-15, 99-29, 00-9, 00-16, 00-22,	Crutchfield J	
	00-34, 01-12, 02-14, 03-7, 03-22, 03-24, 04-1, 04-15, 05-9, 05-20		95-12, 95-19, 96-23, 00-10, 02-8, 02-13, 02-20, 04-22, 04-23, 05-13, 06-13
Chesterfield BP-	80-13, 81-7	Culver JF	
Chiles WD	71-28, 72-5, 72-11, 72-19, 72-21, 74-10, 75-10, 75-14, 76-1, 76-11, 77-15, 77-17, 78-19, 78-33, 78-34, 79-7	,	D
Chittum CB	89-14, 92-27, 95-22, 96-18, 98-2, 98-3, 99-10	Darley JT Darden EB Jr	77-25, 78-35, 82-11, 84-2 78-8
Chubb GP		Dark SJ	76-10, 78-25, 80-19, 83-5, 84-9, 85-9,
Cierebiej A	•	D LAD	86-7, 90-5
,	66-5, 66-26, 66-34, 69-19	Dattel AR	
Clough DL		Daugherty JW-	
	62-2, 62-3, 63-31, 65-19, 65-22, 67-1, 68-14, 71-30, 71-36, 71-40, 72-18, 72-22,	-	63-12, 68-15, 68-18, 70-8, 77-17, 78-20, 78-25, 80-8, 84-4, 85-12, 90-7
	72-33, 73-7, 74-2, 74-7, 74-8, 75-3, 76-6	Davis HV	
Coffey JD		Davis J	
Colangelo EJ		Dean MA	
<u> </u>		Deimier JD	94-21, 94-22, 94-23

Author	Report Number	Author	Report Number
DeJohn CA	- 97-2, 97-21, 00-13, 04-16	England HM	89-10, 92-18, 92-22, 93-6, 94-10
Delafield RH	- 69-12	Enos RJ	99-24
Della Rocco PS	- 89-6, 90-13, 92-30, 95-12, 95-19, 96-23, 99-2, 00-10, 00-32	Ericson SC	04-7, 06-27
Deloney JR	- 83-7		F
deSteiguer D	-78-4, 80-18, 83-10, 83-14		<del>-</del>
· ·	- 02-8, 02-13, 02-20, 02-24, 03-20, 03-11, 05-24, 06-7, 06-18	Faaborg T Fairlie GW	
DeWeese R	- 92-20, 93-14, 94-19, 95-30, 98-11, 02-11, 03-9, 04-18		96-13, 97-4, 98-24, 99-16, 00-3, 01-4 78-8, 82-12, 92-2
Diehl AE	- 87-6	Feinberg R	
Dill DB	- 63-33	Ferrante A	
Dillard A		Ferraro DP	
	-62-12, 63-2, 63-21, 63-24, 63-27, 66-14,		00-32, 01-11, 02-23
Dine jit	66-27, 68-8, 68-16, 72-1, 74-1, 76-7, 77-1,	Fineg J	
	77-20, 79-19, 80-11, 81-1, 81-14, 83-1,	0-	66-6, 66-11, 66-14, 66-41, 68-4, 68-15,
Dillon RD	83-18, 84-7, 87-1 - 81-7		68-23, 70-8, 70-18 71-11 71-15 71-23 71-41
Dittmar MJ		Fisher RG	
Dobbins L		Flemig JW	
Dodd RS		Flux M	77-3, 77-16, 82-5
	- 87-4, 90-8, 94-13, 96-21, 97-17, 02-9,	Folk ED	70-18, 72-30, 73-10, 82-8, 92-27
Dollar Co	03-14, 04-21, 06-30	Forster EM	06-5
Domino D		Fotouhi CH	96-6
Donnelly SS		Fowler PR	63-8, 67-5, 75-7, 77-17, 80-10, 83-2
•	- 97-22, 98-16, 01-16, 02-1, 02-22	Fox CM	01-10, 02-4
Downey LE		Freud SL	64-9, 64-10, 64-17, 66-25
Drechsler GK		Friedberg W	71-26, 78-8, 80-2, 82-12, 92-2, 00-33,
Drilling HS	- 03-23		03-16, 05-14
	- 97-3, 97-23, 98-7	Fromhagen C	
Druray CG		Fulk GW	
Dubowski KM		Fuller DK	
Duke F		Funkhouser GE	63-25, 66-14, 67-4, 67-17, 68-13, 68-15,
Duncan JC			68-18, 70-5, 71-2, 71-17, 72-17, 73-22, 75-10, 75-14, 76-11, 77-8, 77-17, 78-19,
-	- 98-26, 99-3, 00-5, 01-16		79-10, 80-10, 81-8, 82-10, 83-2, 83-14, 85-10, 87-2, 89-8, 89-11, 91-6, 92-27, 95-20, 95-22, 96-18, 98-3, 99-10
Eanuel TW Jr	_		G
Earley JC	- 62-7	Calarry SaiCa	02 5 02 15 0/ 12 05 1/ 0/ 2
Eddington DL	- 06-10	Galaxy SciCorp- Galerston EM	93-5, 93-15, 94-12, 95-14, 96-2
Edwards MB	- 92-31, 94-3, 95-4, 95-9		
Elam GW	-73-17, 81-16, 82-19	Ganslen RV	•
Emanuel T	- 97-11	Garber M	
Emerson TE Jr	- 62-18, 63-1, 63-16, 63-22, 66-11	Garner JD	62-1, 62-9, 65-7, 66-42, 70-19, 72-30, 77-11, 78-3, 78-23, 79-22, 80-12
Endecott BR	-70-3, 77-9, 77-19, 83-12, 85-4 86-1 86-3 86-5 89-4, 90-15, 90-16, 91-17, 93-7, 93-8,	Garner RP	94-10, 95-17, 95-29, 96-4, 97-7, 98-4, 98-27, 99-4, 00-6, 04-3, 04-7, 05-18, 06-10, 06-27
n 11 300	94-7, 94-18, 00-21	Gay DJ	77-24
Endsley MR	- 94-2/, 9/-13	Geiwitz KL	00-6

Author	Report Number	Author	Report Number
George MH	91-2, 91-3, 95-20, 95-22, 95-25, 96-18,	Hastings J	06-1
_	98-3, 99-5, 99-10	Hattrup RA-	05-11
Gerathewohl S	SJ 69-17, 69-24, 70-9, 71-10, 71-33, 75-5,	Hau G	06-10
	77-6, 78-16, 78-27	Hauty GT	65-5, 65-6, 65-16, 65-28, 65-29, 65-30
Gerke RJ		Hawkes GR-	62-11, 62-16
	68-8, 69-9, 69-10, 71-18	Heil MC	99-18, 99-23, 00-12, 01-5, 01-4, 01-6,
Gilcher RO			02-24
Giles E		Heil SKR	01-4
	93-13, 97-5, 97-25, 99-20	Hellman CM	1 91-15, 92-13, 93-18
	71-20, 71-34, 72-34	Hendrix AM	03-13, 95-15, 06-25
Gogel WC	62-15, 63-10, 63-20, 63-28, 64-13, 65-11,	Hendrix R	06-25
C II DE	65-32, 66-22, 66-24, 67-18, 67-20	Higgins EA -	63-23, 66-14, 66-39, 68-13, 68-15, 68-18,
Goldman RF			69-10, 70-5, 70-8, 71-17, 71-41, 72-17, 73-22,
	02-23, 04-22, 04-23, 06-4, 06-26		75-10, 75-14, 76-11, 77-8, 77-17, 78-5, 78-19, 79-10, 79-20, 80-9, 80-10, 81-8, 82-10,
Good GW			83-2, 83-4, 83-14, 85-5, 85-10, 85-11, 87-2,
	71-5, 72-16, 73-19, 76-4, 81-4, 83-17		87-5, 89-5, 89-8, 89-10, 89-11, 89-12
Gowdy RV	90-11, 92-20, 93-14, 94-19, 98-11, 99-5,	Hill RJ	71-39
Carra DM	02-11, 03-9	Hill TJ	93-19
*	77-8, 78-13, 80-3, 81-15, 82-15, 85-8	Hillman DJ -	94-22
-	72-16, 73-19, 75-4, 76-4	Hilton Systen	ns Inc94-20
	72-1, 74-1, 87-1	Hilton TF	97-8, 97-12, 99-19, 00-3
	97-22, 98-16, 01-16, 02-1, 02-22	Hinshaw LB	62-18, 63-1, 63-16, 63-22, 63-26, 63-32,
	67-6, 67-7, 71-20, 71-34, 72-34		66-11
Guilkey JE		Hodges BE	03-10
Gurman EB	94-21	Hoffman SM	1 69-12, 72-17, 73-21, 73-22, 74-11, 75-7, 76-13, 77-5
	H	Holcomb K -	02-20, 05-24, 06-7 06-18
Hadrwarth C	A 98-26, 99-3, 03-10, 03-11, 04-22, 04-23,	Holland J	02-21
T Tackworth Ca	05-13, 06-7, 06-13, 06-18	Holloway FA	94-24
Hand DK	97-3, 97-23, 98-7	Holmes DD	63-23, 63-26, 66-11
	D 70-3, 77-8, 78-8, 81-11, 84-5, 87-3, 87-8	Hordinsky JF	R 91-2, 91-3, 92-11, 92-19, 92-23, 94-14,
	68-6, 68-24, 69-5, 69-13		94-16, 95-28, 97-2, 98-10, 00-21
Hansrote RW		Houk VN	64-7
	81-1, 83-1	Houston ER	98-5
Harper CR		Hudgins CB	98-4, 98-27
1	95-3, 95-7, 96-16, 97-24, 99-22, 05-7,	Hudson LS	90-7
Tiams Tie ji	05-12	Huffine EF	92-24, 92-25, 99-15
Harris JL	84-7	Huffman HV	W 64-15
Harris RM		Hufnagel CA	· 64-7
Harrison HF-	66-16, 70-21	Huggins ME	04-1, 06-14
Hart IS		Hulin CL	97-11, 03-3
Hartel CEJ		Hunter CE	65-31
Hartel GF		Hunter DR -	95-27, 96-19, 97-3, 97-6, 97-16, 97-23,
Hartman S			98-6, 98-7, 99-7, 02-17
	62-7, 62-9, 62-13, 65-14, 66-32, 68-12,	Huntley MS	Jr 91-7, 91-13
- 1400100H 1H1	68-22, 70-7, 71-24, 72-9, 72-27, 73-9,	Hurst MW	78-39
	73-23, 75-12, 77-24	Hutto GL	72-24, 77-21, 81-5
		Hyde AS	63-30

Author	Report Number	Author	Report Number
Hyland DT -	94-21, 94-22, 94-23	Kirkbride L	A 96-19
Hynes MK	99-30, 00-11	Kirkham W	/R78-13, 80-3, 80-6, 81-10, 81-15, 82-7, 82-13, 83-8
	I	Knecht W-	02-20, 05-7, 05-15
	- 	Knowlan D	M 64-11
Iampietro PF	G 62-5, 62-18, 63-1, 63-23, 66-14, 66-23,	Kochan JA	97-6
	68-15, 69-10, 70-8, 70-22, 71-2, 71-4, 71-17, 72-17, 72-35, 75-10, 75-14	Korty P	62-10, 63-4
Ice J		Kot PA	64-11
2	73-13, 73-20	Kranz G	70-10
	02-12, 03-21	Kupfer DM	[ 00-16, 06-14
	I	Kupiec TC	92-24, 96-14, 96-17, 97-14
Jack DG	03-10, 04-22, 04-23, 05-13, 06-20		L
-	99-9, 00-4	Lacefield D	J 78-31, 82-15, 85-8
Jeffress LA		Lacey DE	62-10, 63-4
Jenkins CD -		Lacy CD	71-5
-	69-10, 69-14, 72-5, 72-11, 72-21, 75-10,	LaJonchere	CM 99-28
Jenningo I II	75-14, 76-1, 76-11, 77-17, 78-19, 78-33,	Lamb MW	96-3
	78-34, 78-37	Lambrou P	99-22
Jennings R	06-1	Lamonica J	00-26
Jensen RS	96-19, 97-6, 98-6, 99-7	Langston El	D 72-6, 72-7
Johansson J -	02-1, 02-22	Larcher JG	00-13, 02-16, 04-12, 04-16
Johnson RD	00-20, 02-15, 03-18, 03-23, 04-4, 04-13, 05-10, 05-11, 06-3, 06-5, 06-17, 06-19	Lategola M'	T 63-11, 66-16, 66-17, 66-20, 66-21, 70-8, 70-18, 70-21, 71-8, 71-19, 72-20, 72-26,
Johnson WB	91-16		73-10, 74-6, 77-3, 77-16, 78-5, 78-20, 79-8
Jones D	06-1		79-20, 80-9, 81-2, 82-3, 82-4, 82-5, 84-4
Jones JP	92-31	,	71-36, 72-22
Jones KN	71-5, 71-7, 71-29, 72-14, 72-16,72-25,	Layne PJ	
	73-14,75-1	1	95-31
	82-14, 06-1	_	73-23
Josenhans W		Lendrum L	
Joseph KM	99-9, 99-17, 99-25, 99-27, 00-4, 00-14, 03-2		)75-4, 77-24
	V	1	76-14
	K	Lester LF	
Kanki BG	96-10	_	r 63-30
Karim B	72-27		78-7, 78-36, 79-3, 79-14
Karson S	70-14	Lewis MF -	67-8, 67-16, 67-24, 68-20, 68-27, 70-15,
Kay EJ	94-21, 94-22, 94-23		71-27, 71-32, 71-42, 72-29, 73-6, 73-12, 73-18, 75-6, 79-4, 81-6, 82-6
Keen FR		Lewis RA	69-6, 69-16
Kegg PS	88-3		99-15, 00-20, 00-29, 02-15, 03-18, 03-23,
Kendall WW		1 2 2 2 2 3	04-4, 04-13, 04-15, 05-8, 05-10, 05-11,
Key OR	97-21		06-3, 06-5, 06-12, 06-17, 06-19
Kidd GD Jr -		Li G	, · •
King RE	02-23, 02-24, 03-20, 06-16		P 98-20
	03-11, 04-22, 04-23, 05-13	Linder MK	80-11
Kinn JB		Lintern G -	97-11
,		Lia TL	05-8

Author	Report Number	Author	Report Number
Liu RH	05-8	Melton CE Jr	63-5, 64-18, 66-35, 66-39, 67-15, 68-26,
Loewenfeld I	65-9		69-1, 69-12, 71-2, 71-21, 71-23, 72-17,
Lofberg MS	83-16		73-15, 73-21, 73-22, 74-11, 75-7, 76-2, 76-13, 77-5,77-23, 78-5, 78-18, 78-40,
Loochan FK	91-14, 92-14		79-20, 80-9, 80-16, 81-13, 82-17, 85-2,
Lowenstein O	65-9		86-2, 89-13
Lowrey DL	72-6, 77-11, 78-3, 79-22, 80-12, 80-13,	Melton RJ	79-23
	82-7, 82-13, 83-8	Mertens HW	65-32, 66-22, 66-38, 67-20, 67-24,
Luchsinger PC	64-8		68-27, 70-15, 71-42, 72-29, 75-6, 77-12,
Lyne PJ	63-8, 73-10, 77-3, 77-16, 78-20, 81-2, 82-3, 82-4, 84-4, 85-10, 87-2, 89-8, 89-10, 89-11, 89-12		78-15, 79-4, 79-25, 81-6, 81-8, 82-6, 82-10, 83-4, 83-15, 85-3, 85-5, 88-2, 90-9, 92-6, 92-28, 92-29, 92-30, 93-16, 93-17, 95-13, 96-22, 97-10, 90-8, 94-14
Lynn CA	73-10	M. DA	93-17, 95-13, 96-22, 97-10, 99-8, 04-14
		Mielnik T	67-2, 68-7, 70-10, 71-5
	M		06-10 82-10, 92-28, 92-29, 92-30, 93-16,
Maclin O		Milburn INJ	93-17, 95-13, 96-22, 97-10, 99-8, 04-10, 04-14, 06-26
Madakasira S		Milke RM	
	95-29, 98-4, 98-27, 05-18	Millett DP	// <del></del>
Manning CA	84-6, 88-3, 89-6, 90-4, 90-6, 90-13, 91-9, 92-5, 92-26, 92-31, 94-3, 94-9, 95-4, 95-9,		97-7, 98-15, 00-30, 01-10, 01-16, 02-1,
	96-5 97-15, 97-22, 98-16, 98-26, 99-3,	1711110 011	02-2, 02-4, 02-22
	00-2, 00-5, 01-5, 01-6, 01-10, 02-2, 02-4,	Mills W	01-11
	05-4, 06-4, 06-21, 06-29	Moertl PM	00-5, 02-1, 02-22
	93-14, 94-11, 96-7, 96-11, 97-18, 97-20	Mogford LS	98-14
Marsh DK II		Mogford RH	98-14
Mastrullo AR		Mogilka HJ	01-10, 02-4
Masucci FD		Mohler SR	62-4, 62-20, 63-2, 65-7, 65-13, 66-1,
	72-18, 72-22, 72-33, 73-7, 74-2, 74-7, 75-3		66-3, 66-8, 66-25, 66-29, 66-30, 66-31,
May ND			66-32, 67-22, 68-8, 68-16, 69-2, 69-17, 69-18, 70-12, 71-9, 71-10, 71-33, 72-2,
McCauley ME			72-28, 75-5, 80-4, 96-25, 06-1
McClenathan JE		Moise S	
McConville JT -		Montgomery RW	793-21, 94-15, 95-11, 96-12, 99-6, 00-19,
McCoy J			00-23, 01-7, 01-14, 02-6, 02-10, 03-6,
McDown JR			03-12, 04-6, 04-9, 05-21, 06-9, 06-23, 06-28
McFadden EB	62-13, 62-21, 63-9, 65-7, 66-7, 66-13, 66-20, 67-3, 67-4, 67-9, 70-20, 71-37,	Moorcroft D	
	72-10, 78-1, 78-4, 78-9, 79-13	Moore CM	
McKenzie JM	63-8, 66-41, 67-5, 71-2, 71-21, 73-21,	Morgan JC	
-	73-22, 74-11, 75-7, 75-10, 75-14, 76-11,	Morris Edward W	
	76-13, 76-15, 77-17, 77-23, 78-18, 78-19, 78-20, 78-40, 70-10, 70-20, 80-10, 81-8	Morris Everett W	
	78-30, 78-40, 79-10, 79-20, 80-10, 81-8, 81-13, 82-10, 83-2, 83-4	Morrison JE	
McLean GA	89-8, 89-10, 89-11, 89-12, 91-12, 92-18,	Morrow DG	
1/10230001 30 1	92-22, 92-27, 93-6, 93-19, 95-22, 95-25,	Moser E	
	96-18, 98-2, 98-3, 98-19, 99-5, 99-10,		64-5, 64-7, 64-8
161. 1	01-2, 02-16, 03-15, 04-2, 04-12, 04-19		66-14, 68-4, 71-11, 71-15, 80-10
McLin L			77-17, 78-19, 79-10
Mehling KD		Murcko LE	
Mejdal S	01-1/		98-4, 98-27, 00-6
		1 * '	90-2, 91-5, 91-10, 92-15, 92-16, 95-10
		111,010 ) (	

Report Number

Author

Author	Report Number	Author Report Number
	N	Parker JF Jr 89-9, 90-14, 95-2
		Patterson JC 01-11
Naff KC		Pearson DW 68-17, 69-7, 69-19
Nagle FJ	63-12, 63-34, 64-2, 66-36	Pearson RG 63-35, 65-10, 65-31, 66-19
Nakagawara V	VB 90-10, 91-1, 91-14, 92-14, 93-11, 93-21,	Pendergrass GE 63-27, 66-10, 66-15
	94-10, 94-15, 95-11, 96-12, 96-27, 98-25, 99-6, 00-18, 00-19, 00-23, 01-7, 01-14,	Penland T 85-1
	02-6, 02-10, 03-6, 03-12, 04-6, 04-9,	Pennybaker AL 96-25
	05-21, 06-9, 06-23, 06-28	Perloff JK 64-19
Nance C	00-26	Perry JL 98-16
Naughton J -	64-2, 66-17, 66-21, 66-36	Perry RB 64-8
Neal GL	65-31	Peterson LM 00-28, 01-19, 01-20, 03-10
Neas BR	78-8, 80-2	Pfleiderer EM 00-24, 01-10, 02-2, 02-4, 03-8, 05-16,
Neddick M	99-9	06-4, 06-7, 06-29
Nelson JM	71-26	Phillips EE 63-34
Nelson PL	72-33, 73-7, 74-8	Phillips S 97-11
Nesthus TE -	95-5, 95-7, 97-7, 97-9, 97-25, 99-20, 02-8,	Pickett E 98-20
	02-13, 02-20, 06-13	Pickrel EW77-25, 79-18, 82-11, 83-11, 84-2
Newton JL		Pidkowicz JK 80-8
Newton NL-		Pinkerson AL 64-11
Nguyen K		Pinski MS78-4, 78-14
Nicholas J		Podolak E 65-25, 68-3
Nichols EA		Polis BD71-2, 73-21, 73-22
Nikolic D		Pollard DW 78-3, 79-6, 79-23, 82-8, 84-1, 85-1
	X71-25, 71-38, 82-14	Porter KA 02-16
Nye LG	89-7, 90-4, 90-8, 91-8, 92-7, 92-8, 92-9, 92-10, 94-13	Pounds J 99-12, 02-12, 03-19, 03-21, 05-5, 05-25 06-20, 06-21, 06-26
	•	Price GT 69-3, 69-13, 74-4, 77-8
O'Brien K	<b>U</b> 00-33	Prinzo OV 93-20, 95-15, 96-10, 96-20, 96-26, 98-1 98-20, 99-21, 01-8, 01-9, 02-5, 03-13, 04-11, 05-19, 06-25
O'Connor W	T 65-10, 66-10, 66-15	Purswell JL72-27, 73-23
O'Dell JW	70-14	72 27,73 23
O'Doherty D	OS 65-4	0
Odom RS	02-16	_
O'Donnell R	D 92-11, 95-24	Quebe J 97-3, 98-7
Ohrt DD	97-22, 98-16	D
Olmos BO	03-2	R
Orme DR	01-11	Raeke JW 62-21
Orzechowski	JA 04-7, 06-27	Ramos RA 01-5, 01-6
OU Vortac	92-31, 94-3, 95-4, 95-9, 96-5	Rana B75-9
Owuor ED	04-1	Rantanen E 03-3
Ozur H	82-11 <b>P</b>	Rasmussen PG 70-7, 71-24, 72-9, 73-9, 75-12, 77-2, 77-7, 77-13, 77-14, 78-17, 78-22, 78-28, 78-29, 78-41, 79-22, 80-13, 81-7, 89-14, 92-12, 94-8
	<u>-</u>	Reed W72-6, 73-1
Packingham 1		Reighard HL 65-3, 76-8, 78-35
Page BB		Reins DA 63-26, 65-27, 66-11
Palmerton Da	A 98-3, 98-13, 02-16, 04-12, 05-17	Retzlaff PD 03-20

Report Number

Author

Author	Report Number	Author	Report Number
Revzin AM	70-11, 73-3, 73-4, 77-22, 78-2, 79-15,	Scarpa P	06-1
	92-12, 94-8	Schlegel RE -	93-13, 97-5, 97-25, 98-13, 99-20
Reynolds HI -		Schlegel TT -	89-10
Reynolds HM	[ 75-2, 75-13, 76-9, 82-9	Schroeder D	J 68-10, 70-10, 71-6, 71-16, 71-20, 71-31,
Rice N	70-10		71-34, 71-39, 72-34, 73-17, 79-9, 81-16,
Rieger JA Jr	66-11		82-19, 83-7, 83-17, 87-4, 89-7, 90-6, 90-8, 92-7, 93-4, 94-6, 94-13, 94-17, 94-26,
Ritter RM	93-7, 93-8, 94-7, 98-18, 98-21, 03-23		95-3, 95-7, 95-32, 96-9, 97-17, 99-17,
Rizutti BL	76-6		99-22, 00-32, 03-14, 03-20, 04-21,05-5,
Roberts PA	78-31, 82-15, 85-8		05-22, 06-2, 06-6, 06-21
Robinette KM	1 83-16	Schvaneveldt	: R 00-26
Robinson CP	77-19, 78-26	Scow J	66-15
Robinson S	63-33	Seipel JH	64-6, 65-4, 67-11
Rock DB	82-11	Sells SB	84-2
Rodgers MD-	93-1, 93-9, 93-12, 93-22, 94-27, 95-16,	Sershon JL	84-5, 87-3, 87-8
_	95-18, 97-13, 98-14, 06-20	Shaftstall RN	1 02-16, 06-10, 06-19
Roe BA	00-16	Shanbour K-	66-17, 66-21
Rohrbaugh JV	W 99-28	Shappell SA -	00-7, 01-3, 03-4, 05-7, 05-24, 06-7, 06-18,
Rosa RR	95-32		06-24
Rose RM	78-39	Shaw RV	96-24
Ross A	67-22	Shehab RL	98-13
Rotter AJ	92-31	Shepherd W	Τ 89-9, 90-14, 91-16, 95-2, 95-14, 95-31,
Rowlan DE	72-15		96-2
Rowland RC	Jr 67-10		67-25, 68-9, 69-2, 69-17, 69-18, 71-10
Roy KM	02-19	Silberman W	
Rubenstein C	J 93-19	Simcox LS	
Ruehle C	06-1		66-13, 67-9, 78-13, 80-3
Rueschhoff B	J 85-11	Simpson LP-	81-4
Rush L	97-9	Sirevaag EJ	
Russell CJ	00-15		70-9, 72-3
	85-12, 89-3	Smith DR	00-9, 00-21, 02-14, 00-34
Ryan LC	70-3, 75-5, 80-4	Smith LT	93-19
Rylander R			98-5, 98-21
,		Smith PW	62-8, 63-24, 69-9, 70-3, 77-9, 77-19, 78-26
cl: r	\$	Smith RC	70-20, 71-14, 71-21, 71-28, 71-30, 71-35, 72-23, 72-24, 73-2, 73-15, 73-22, 74-12, 75-7, 75-9, 76-2, 76-13, 77-21, 77-23,
Sahiar F			73-7, 73-3, 76-2, 76-13, 77-21, 77-23, 78-32, 79-11, 80-14, 81-5
-	97-21, 06-1, 06-12	Snow CC	62-9, 65-14, 65-26, 68-6, 68-19, 68-24,
Saldivar J 1	75-7, 76-13, 77-5, 77-23, 78-18, 78-40, 80-18, 81-13 83-10, 83-14, 85-10, 87-2		69-3, 69-4, 69-5, 69-13, 70-16, 72-27, 75-2, 79-2, 82-9
Sanders DC	67-21, 70-4, 70-13, 72-12, 77-9, 83-12,	Snyder L	77-8, 82-12, 92-2
ounders B C	85-4, 86-1, 86-3, 86-5, 86-8, 89-4, 90-15, 90-16, 91-17, 93-7, 93-8, 94-7, 94-18, 95-8, 98-10	Snyder RG	62-13, 62-19, 63-15, 63-30, 65-12, 65-26, 68-6, 68-19, 68-24, 69-3, 69-4, 69-5, 69-13, 76-9
Sangal SP		Solomon LA	66-11
Sauer HH		Soper JW	96-17, 99-29, 00-16, 02-14, 03-22, 03-24
Scarborough A		Southern TL	
_	WR 64-12, 65-8, 65-15	Spera S	
	······	Spieth W	
	Spieth	-r ''	

Author	Report Number	Author	Report Number
St George R-	99-9	Truitt TR	96-5, 98-26, 99-3, 00-5
Staggs CM	85-6	Tucker R	00-26
Stavinoha W	B 66-11	Turner JW -	91-7, 91-13
Stedman VG	71-9	Twohig P	04-22
Steen JA	71-27, 71-32, 72-29, 73-18, 75-1, 75-6, 80-5, 80-15, 84-1, 85-1	Tyler RR	02-21
Stern JA	94-6, 94-17, 94-26, 96-9, 99-28		U
Stoliarov N	94-6, 94-26, 96-9		•
Stutzman TM	1 91-5	1	02-3, 03-5
Swearingen J	J 62-1, 62-4, 62-13, 62-14, 63-9, 65-7,		L66-25
0 22	65-20, 65-23, 66-3, 66-12, 66-18, 66-40, 67-14, 69-22, 71-3, 71-12, 71-13, 72-6, 72-7, 72-15, 73-1	1 2	PP69-20 04-3
	T		V
T-: C	05.22		77-4, 90-12
Taite S			elen AG-65-8
	97-11, 03-3		LK80-5, 80-15
Tang PC		Vance FP	68-26
•	75-9, 81-15, 83-6, 84-6		er AD80-7, 83-6, 84-6
-	97-11, 03-3	Vant JHB	89-5
Taylor JC		Vardaman J	J94-5
Teague SM		Vaughan JA	68-13, 68-15, 68-18, 69-10, 70-5, 71-17,
Thackray RI	68-17, 69-7, 69-8, 69-21, 71-7, 71-29, 72-14, 72-25, 73-11, 73-14, 73-16, 74-9, 75-8, 77-18, 78-11, 79-12, 79-24, 80-1, 80-17,		72-17, 75-10, 75-14, 76-5, 76-11, 77-2, 77-7, 77-13, 77-14, 78-17, 78-22, 78-28, 78-29, 78-41, 79-20, 80-9
	81-5, 81-12, 82-1, 82-16, 83-13, 85-13, 86-4, 88-1, 88-4, 89-1, 90-3, 92-3, 92-6, 94-6	1	AB99-28
Thomas AA -	71-41	00 -	66-25, 67-22, 67-23
Thomas JA	06-10	veronneau S	6JH94-14, 95-5, 96-25, 97-2, 00-13, 00-18, 00-22
Thomas S	05-8	Ververs PM	98-28
Thompson D	) 06-20		erg CW-66-31
Thompson JJ	· 00-3		94-22
Thompson K			94-7, 98-18, 99-14, 00-16, 04-1, 04-4,
Thompson R	.C 97-8, 97-12, 98-8, 98-24, 99-17, 99-19, 99-24, 99-25, 99-27, 00-14, 00-17, 00-25, 00-27, 00-28, 01-4	VUIVI	06-14 W
Thomson GI	2 97-22		W
Tilton FE		Wade K	01-15, 05-1, 05-3
	63-7, 63-17, 63-19, Tech. Pub.#1, 64-16,	Wallace TF-	69-22, 72-15, 78-13, 80-3
,	65-17, 66-4, 67-10, 68-21, 68-25, 70-6,	Wang SM	05-8
	71-1, 72-31, 72-32, 73-13, 73-20, 75-11,		92-11
Touchstone F	76-3, 79-5, 79-16 RM 69-21, 71-29, 72-14, 72-25, 73-11, 73-14,	Wayda ME-	90-1, 92-1, 94-1, 96-1, 97-1, 98-1, 99-1, 00-1 01-1, 03-1, 05-1
	73-16, 74-9, 75-8, 77-18, 78-11, 79-12, 79-24, 80-17, 81-12, 82-1, 82-16, 83-13, 85-13, 86-4, 88-1, 89-1, 90-3, 92-6, 94-6, 94-26, 96-9		DA90-7, 05-24, 06-7, 06-18, 06-24 JJ97-3, 97-23, 98-7
Trent CC			76-5, 77-2, 77-7, 77-13, 77-14 78-17
	61-1, 62-3, 63-31, 65-5, 65-6, 65-21, 65-22		78-22 78-28 78-29 78-41
	78-6, 78-12, 78-24, 79-17	Wentz AE	64-1, 64-6
		Wernick JS-	63-19

Author Report Number Author Report Number West G -----71-17, 72-5, 72-19, 72-21, 74-10, 75-14 X West RW -----91-1 Xing J-----04-17, 05-4, 06-2, 06-6, 06-11, 06-15, Westura EE -----68-3 06-22Wheelright CD ----62-1 Whinnery JE -----03-15, 04-1, 05-20, 06-1, 06-5, 06-12 White MA -----83-2 White ME -----82-10 Yanowitch EA ---- 73-5 White VL -----92-23, 94-16, 96-14, 96-17, 00-22, Yanowitch RE ---- 72-2, 73-5 01-12, 04-1 Yost A----- 02-21 Wick RL Jr----72-4 Young CL ---- 76-6 Wickens CD-----98-28 Young FA----- 79-2 Wicks SM------66-35, 66-39, 67-15, 68-26, 69-1, 77-23, Young JW ----- 62-21, 65-23, 66-9, 66-33, 67-13, 69-3, 78-18, 78-40, 80-10, 81-13, 82-7, 82-13, 83-8 69-4, 69-5, 69-13, 71-37, 74-4, 76-9, 78-14, 82-9, 83-16, 89-8, 89-11, 93-10 Wiegmann DA 01-3, 03-4, 05-24, 06-7, 06-18, 06-24 Wilcox BC Jr ---- 91-12, 92-18, 92-22, 93-6, 94-10, 96-25 Young PE----- 68-11, 68-12 Young WC ----- 93-4, 96-13, 97-4 Willems BF ----- 01-20, 02-18 Williams CA----- 00-14, 03-10, 03-17, 04-20 7 Williams CA---- 02-24 Williams KW----- 94-25, 95-6, 96-8, 98-12, 99-13, 99-26, Zehner GF ----- 83-16 00-8, 00-28, 00-31, 01-13, 02-21, 04-20, Zeiner AR-----72-8 04-24, 06-8 Zelenski JD ---- 77-19 Williams MJ ---- 69-15 Zhu H ----- 04-1 Williams SD ---- 03-23 Ziemnowicz SAR 65-4 Willis DM ----- 75-12 Wing H ----- 91-9 Winget CM----- 75-10 Wise RA----- 97-7 Witt LA ----- 91-10, 91-11, 91-15, 92-7, 92-8, 92-9, 92-10, 92-13, 92-17, 92-21, 93-18, 94-2, 95-32, 97-8 Wittmers LE----- 65-27 Wolbrink AM ---- 04-16, 00-13 Wolf MB ----- 98-4 Wong KL----- 04-7, 06-27 Wood KJ ----- 91-14, 92-14, 93-11, 93-21, 94-15, 95-11, 96-27, 98-25, 99-6, 00-19, 01-14, 02-6, 02-10, 03-6, 04-6, 06-9, 06-23, 06-28 Worley JA ----- 99-17, 99-25, 99-27, 00-14 Wreggit S----- 97-9, 98-9

# PART III: SUBJECT INDEX

Subject and Report Number

Subject and Report Number

## Acceleration, angular

- ...adaptation, 66-37, 67-6, 67-7, 67-12, 67-19, 69-20, 74-3
- ...antimotion sickness drugs effects, 81-16, 82-19
- ...alcohol effects, 71-6, 71-16, 71-20, 71-34, 71-39, 72-34, 95-3
- ...arousal effects on nystagmus, 62-17
- ...arousal effects on vestibular response, 63-29
- ...dextroamphetamine effects on performance, 73-17, 76-12
- ...nystagmus after caloric habituation, 63-14, 64-14, 65-18, 67-2
- ...nystagmus after rotation habituation, 63-13, 65-24, 68-2
- ...rotation device, 64-15
- ...secobarbital effects on performance, 73-17
- ...sleep loss effects on performance, 76-12, 86-9

## Acceleration, linear (see also Deceleration)

...bibliography, 63-30

## Accidents

- ...age of pilots, 77-10, 04-8
- ...agricultural aircraft, 66-27, 66-30, 72-15, 78-31, 80-3
- ...Alaskan CFIT, evaluated by HFACS, 00-28, 06-7 ...alcohol involved, 66-29, 68-16, 78-31, 80-4,
- 92-24, 98-5, 00-21, 03-18, 03-23, 04-13, 05-20
- ...analyses of injuries, 70-16, 71-3, 72-15, 81-10, 82-7, 05-17
- ...analytic methodology of causal factors, 06-26
- ...bloodborne pathogens, 97-21
- ...cabin injuries, 79-23, 82-8
- ...carbon monoxide levels without fire, 80-11, 00-18, 00-34, 05-9
- ...cocaine and associated metabolites, analytic method, 03-23, 03-24
- ...causes, 66-8, 66-27, 66-29, 67-23, 68-16, 69-2, 70-18, 78-13, 82-15, 05-9, 05-20, 05-24, 06-24
- ...cockpit delethalization, 66-3, 66-12, 71-3
- ...controlled flight into terrain, human error analysis,
- ...coronary atherosclerosis in pilot fatalities, 80-8, 85-6
- ...drugs and toxic chemicals as causes, 68-16, 78-31, 85-8, 95-28, 96-17, 00-9, 00-21, 00-29, 00-34, 03-7, 03-22, 03-23, 03-24, 05-20
- ...evacuation injuries, 79-6, 80-12, 99-30, 00-11
- ...evacuation patterns, 62-9, 65-7, 70-16, 96-18
- ...experience of pilots, 77-10

- ...fatalities identification, 79-2, 98-18, 06-14
- ...fire, smoke protection, 67-4, 70-16, 70-20, 78-4, 83-10, 85-10
- ...glare involvement, 03-6, 06-28
- ...glucose levels, abnormal, 00-22
- ...HFACS, human factors analysis and classification system for human error, 00-7
  - –applied to air carriers and commuter accidents,06-18
  - -applied to Alaskan CFIT accidents, 00-28
  - -applied to general aviation CFIT accidents, 03-4
  - -applied to general aviation accidents, 1990-2000, 05-24
  - -applied to general aviation accidents in Alaska, 06-7
  - -in conjunction with intervention programs, 06-24
- ...in-flight incapacitation, 87-7, 04-16
- ...in-flight vertigo and unconsciousness, 63-21
- ...injuries, from seat impacts, 66-18
  - -in extreme vertical impacts, 62-19
  - -in rearward-facing seats, 62-7
- ...instructional flights, 96-3
- ...intervention programs, 06-24
- ...investigations, human factors findings, 63-35, 69-18, 72-2, 73-5, 80-6, 04-24, 05-24, 06-24
- ...lapbelt-restraint injuries to pregnant females, 68-24
- ...lost/disoriented, 95-1
- ...occupation of pilots, 77-10
- ...older pilots, 67-22, 70-18, 04-8
- ...padding for crash protection, 66-40
- ...physician pilots, 66-25, 71-9
- ...pilots with static physical defects, 76-7, 77-20, 79-19, 81-14, 83-18, 93-11
- ...post mortem findings, 69-18, 92-23, 92-24, 92-25, 94-14, 95-28, 97-14, 98-18, 00-9, 00-16, 00-29, 03-4, 03-22, 03-24, 04-13, 05-9, 05-10, 05-11,
  - 05-20, 06-3, 06-14, 06-17
  - -in relation to medical history, 06-12
  - -quality assurance of forensic analyses, 99-11, 99-14, 99-15, 99-29, 03-18, 04-1, 04-4, 04-13, 04-15, 06-14
- ...predisposition, 72-2, 73-5, 93-9
- ...prevention with blind flight instrument, 66-32
- ...propeller-to-person, 81-15, 93-2
- ...railroad, 73-1
- ...risk factors, for controlled flight into terrain (Alaska) , 00-28
  - -for marginal weather take-offs by general aviation pilots, 05-7, 05-15

- ...rotorcraft, rollover and injury/fatality rates, 05-17
- ...safety information for improved survival, 04-19
- ...seat cushions for flotation, 66-13, 98-19
- ...shoulder harnesses to increase survival, 72-3, 83-8, 89-3
- ...spatial disorientation, 78-13, 95-1, 96-21
- ...stall warning, 66-31
- ...suicide, 72-2, 73-5, 06-5
- ...survivability, fire/smoke, 95-8, 05-17
  - -free-fall impacts, 63-15
  - -water impacts, 65-12, 68-19
- ...triamterene in blood, identification of, 92-23
- ...unmanned aircraft, accidents and incidents, 04-24 –flight-control problems, 06-8
- ...visual acuity of pilots, 75-5, 81-14, 83-18, 00-18
- ...water spray systems, 98-4
- ...water survival, analysis of training programs, 98-19 –frequency of occurrence, 98-19
- ...WinMine analytic tool applied to accident data, 06-26

## Aerial application

- ...accidents, 66-27, 66-30, 68-16, 72-15, 78-31, 80-3
- ...biochemical effects of lindane and dieldrin, 62-10, 63-4
- ...chlordimeform toxicity, 77-19
- ...cholinesterase determination, 67-5
- ...comparison of serum cholinesterase methods, 70-13, 72-12
- ...dieldrin effects on liver, 66-5, 66-26
- ...endrin effects, 66-11, 66-26, 66-34, 70-11
- ...mechanisms of endrin action, 63-16, 63-26
- ...organophosphate insecticides effects, 63-24, 69-19, 70-3
- ...Phosdrin effects on performance, 72-29, 73-3
- ...Phosdrin effects on vision, 73-4
- ...storage stability of human blood cholinesterase, 70-4
- ...toxic hazards, 62-8, 68-16, 78-31
- ...treatment of methamidophos poisoning, 78-26

## **Aerobatics**

- ...blood donation effects, 84-4
- ...G effects on pilots, 72-28, 82-13

## Aerospace

...medical screening guidance for commercial aerospace passengers, 06-1

#### Age

- ...age 60 rule, 94-20, 94-21, 94-22, 94-23, 04-8
- ...air traffic controller, health, 65-6, 71-8, 71-19,
  - -performance, 61-1, 62-3, 65-21, 67-1, 71-36, 73-7, 84-6, 90-4

- -retirement age, 05-6, 05-22
- ...aircraft accident survival, 70-16
- ...aircraft accidents, pilots involved, 67-22, 70-18, 77-10, 95-11
- ...alcohol and altitude interaction, 88-2
- ...alcohol effects on performance, 95-3, 95-7
- ...aviation personnel, 64-1, 94-20, 94-21, 94-22, 94-23
- ...binocular fusion time effects, 66-35
- ...cardiovascular disease and performance, 64-4
- ...cardiovascular health changes in airmen, 72-26
- ...cockpit visual problems of senior pilots, 77-2, 77-7, 77-13, 77-14, 78-17
- ...complex monitoring performance effects, 81-12, 82-16, 83-15, 85-3, 88-2
- ...index for pilots, 77-6, 78-16, 78-27, 82-18
- ...pupillary reflex relationship, 65-25
- ...shiftwork, 95-19
- ...sonic boom effects during sleep, 72-19, 72-24, 72-35
- ...work capacity, 63-18, 63-33

#### Air ambulance

- ...cardiopulmonary factors in perinatal air transport, 82-5
- ...status of civilian air ambulance services, 71-18

## Air bags

...restraint tests, 69-3, 69-4

#### Air loads

- ...effects on man, 63-9
- ...small-aircraft decompressions, 67-14

## Air piracy

...deterrence, 78-35

#### Air traffic control

- ...ability requirements, 92-26, 98-8, 98-16
- ...Air Traffic Selection and Training (AT-SAT) project, 00-2, 06-16
- ...automation issues, 90-13, 92-31, 94-3, 95-4
- ...blink parameters and display highlighting, 99-8
- ...boredom with simulated radar control, 75-8, 80-1.
- ...Cockpit Display of Traffic Information (CDTI),
- 00-30, 03-2, 03-13, 04-11
- ...cognitive style aspects, 99-12
- ...color highlighting and color deficiency, 92-6
- ...color use in ATC displays, 06-2, 06-6, 06-11, 06-15, 06-22
- ...communications, 96-10, 96-26, 98-17, 98-20, 99-21, 03-13, 05-19, 06-25
- ...conspicuity of colored and flashing targets, 90-3 –target blink amplitudes, 97-10, 99-8
- ...density, warnings, and collision avoidance, 73-6

- ...flight progress strips, use of, 92-31, 94-3, 95-4, 95-9, 96-5, 00-5
- ...information complexity measures, implications for automation design, 04-17
- ...information requirements, TRACON, 95-16
- ...job task taxonomy, 93-1
- ...memory, 97-22
- ...napping and night shift performance, 00-10
- ...noise effects on performance of radar task, 79-24
- ...operational errors, evaluation of the Severity Index, 05-5
  - -evaluation of HFACS and other models to describe causes, 05-25
  - -review of human factors literature, 06-21
- -static sector characteristics, effect on, 06-4
- ...operational errors and incidences, causal factors and the JANUS technique, 03-21
  - -development of temporal markers to profile, 06-20
  - -role of shiftwork and fatigue, 99-2
- ...ophthalmic requirements, 96-12
- ...radar performance with and without a sweepline, 79-12.
  - -with and without computer aiding, 89-1.
- ...radar training facility, 80-5, 80-15, 83-9
- ...resource management, crew, 95-21
- ...SATORI, 93-12, 97-13
- ...sector characteristics, activity and complexity, 06-29
  - -static, and operational errors, 06-4
- ...selection and supervisory training, 92-16
- ...shiftwork, 71-2, 73-21, 73-22, 74-11, 75-7, 76-13, 77-23, 82-17
- ...situation assessment through re-creation of incidents (SATORI), 93-12, 98-14
- ...situation awareness, 94-27, 95-16, 97-13, 98-16, 99-3, 03-2, 03-5, 03-13, 04-11, 04-20
- ...simulator for research, 65-31
- ...systematic air traffic operations research initiative (SATORI), 97-13, 98-14
- ...teamwork, performance feedback in simulation, 00-25
- -teamwork, training platform, 99-24
- ...vigilance at three radar display target densities, 77-18
- ...vigilance of men and women on simulated radar task, 78-11, 80-17
- ...visual displays, cognitive complexity, 05-4
- ...visual taskload effects, on CFF change during complex monitoring, 85-13
  - -on complex monitoring, 88-1, 90-3
- ...voice communications from, 93-20, 98-17, 98-20, 05-19

## Air traffic controllers

- ...age and retirement, 05-6
- ...age effects on performance, 61-1, 62-3, 65-21, 67-1, 71-36, 73-7, 81-12, 82-16, 84-6, 90-4, 96-23, 99-18, 99-23, 05-6, 05-22
- ...aircraft mix and complexity ratings, 05-16
- ...anthropometry, 65-26
- ...anxiety with training, 89-7, 91-8
- ...anxiety with workload, 73-15, 80-14, 81-5
- ...aptitude tests for selection, 65-19, 68-14, 71-28, 71-36, 71-40, 72-18, 89-6, 90-8, 97-15, 98-23, 99-16, 00-2, 06-16
  - -reweighting AT-SAT scores to reduce adverse impact, 06-16
- ...attitudes, 74-7, 74-12, 75-3, 79-11, 91-10, 00-17, 04-23
- ...attrition, 72-33, 74-2, 74-7, 75-3
- ...biochemical stress index, 74-11, 75-7, 77-23, 78-5, 78-40
- ...biodynamic evaluation, 71-8
- ...biographical factors associated with training success, 83-6, 84-6, 90-4, 94-13
- ...biomedical survey, 65-5, 65-6
- ...collegiate training initiative, 98-22
- ...color deficiency in a workforce sample, 06-1
- ...color perception and job performance, 83-11, 90-9, 92-6, 92-28, 92-29, 96-22, 06-2, 06-6, 06-11, 06-15, 06-22
- ...color vision tests, 85-7, 90-9, 92-28, 92-29, 95-13, 96-22, 04-10, 04-14, 06-2, 06-6, 06-11
- ...communication, 93-20, 95-15, 96-10, 96-20, 96-26, 98-17, 98-20, 99-21, 01-8, 01-9, 05-19, 06-25
- ...commuting (driving) risks before and after shifts, 06-13
- ...Composite Mood Adjective Check Lists to measure fatigue, 71-21
- ...disease incidence and prevalence, 78-21, 84-3
- ...education as selection factor, 76-6, 90-4
- ...experience as selection criterion, 63-31, 71-36, 74-8, 00-12
- ...fatigue and shiftwork, 99-2
  - -and commuting risk factors before and after shifts, 06-13
- ...flight progress strips, use of, 92-31, 94-3, 95-4, 95-9, 96-5, 98-26, 00-5
- ...flight service station, training, 86-6, 91-4 –organizational climate, 97-12
- ...headset interference tones, 92-4
- ...health changes, 71-19, 72-20, 78-39, 84-3
- ...height and weight data, errors in, 73-10
- ...incident reporting, 65-10, 03-19
- ...memory, 97-22, 98-16

- ...military experience and selection, 92-5
- ...motivational factors, 71-30, 73-2
- ...Multiple Task Performance Battery for selection, 72-5, 74-10
- ...Myers-Briggs personality types, 04-21
- ...napping and night shift performance, 00-10
- ...NEO Personality Inventory-Revised, compared with 16 PF test, 03-20
- ...occupational vision, 96-12, 96-27
- ...operational errors, evaluation of the Severity Index, 05-5
  - -evaluation of HFACS and other models to describe causes, 05-25
  - -static sector characteristics, influence on, 06-4
- ...operational errors/deviations, 99-2, 03-19, 03-21, 05-22, 06-21
- ...perceptions of aircraft performance, 00-24, 03-8, 05-16
- ...performance evaluation, 61-1, 65-22, 73-7, 93-12, 98-14, 00-2
- ...performance on radar monitoring tasks, 82-1, 83-13, 86-4, 88-1, 88-4. 90-3, 94-26, 95-23, 97-10, 98-16, 99-8
- ...performance during CDTI evaluation, 00-30, 03-2, 03-13
- ...personality factors, and disability retirement, 03-14 –and performance, 70-14, 93-4, 94-13, 04-21
- ...physiological responses, 71-2, 73-21, 73-22, 74-11, 75-7, 76-13, 77-23, 82-17
- ...pilot satisfaction with services, 90-6
- ...presbyopic, 96-12, 96-27
- ...psychological testing, 61-1, 62-2, 80-14, 81-5, 92-30, 97-17, 98-23, 99-16, 99-23, 03-14, 03-20, 06-20
- ...selection, 62-2, 72-33, 74-8, 76-6, 77-25, 78-7, 78-36, 79-3, 79-14, 79-21, 80-7, 80-15, 80-17, 82-11, 83-6, 84-2, 84-6, 88-3, 89-6, 89-7, 90-4, 90-8, 90-13, 91-4. 91-8, 91-9, 91-18, 92-5, 92-26, 94-4, 94-8, 96-6, 96-13, 97-4, 97-15, 97-17, 97-19, 98-23, 99-16, 99-18, 99-23, 00-2, 00-12, 00-15, 03-20, 06-16
- ...sex differences in selection, training, and attrition, 72-22, 74-2, 74-7, 75-3, 96-13, 98-23
- ...shift rotation patterns, effects, 73-22, 75-7, 77-5, 85-2, 86-2, 95-12, 95-19, 96-23, 99-2, 00-10, 06-13
- ...situation awareness, 99-3, 03-2
- ...Sixteen Personality Factor test, air traffic controllers, 97-17, 03-20
- ...sleep patterns, 77-5, 95-12, 95-19, 00-10
- ...stress, 71-2, 73-21, 73-22, 74-11, 75-7, 76-13, 77-23, 80-14, 81-5, 82-17
- ...symptoms reported, 61-1

- ...taskload measures, 01-10, 02-2, 03-8, 05-16, 06-4, 06-29
- ...team work, performance feedback in simulation, 00-25
- ...training, 78-10, 79-3, 79-18, 80-5, 80-15, 82-2, 83-9, 88-3, 89-6, 89-7, 90-4, 90-8, 91-4, 94-9, 94-13, 95-4, 96-6, 98-8, 98-22, 98-23, 99-16, 00-12
- ...voice communications, 93-20, 95-15, 98-20, 99-21, 05-19

## Air transportation

- ...animals, 77-8, 81-11, 84-5
- ...dry ice packaging in air cargo, sublimation rate, 06-19
- ...high risk pregnant women and neonates, 82-5, 00-33, 03-16
- ...human external loads, 98-13
- ...infectious disease substances, 95-29
- ...in-flight medical care, 00-13
- ...in-flight medical incapacitation and pilot impairment, 87-7, 04-16
- ...life preserver retrieval, , 03-9
- ...medical kits, 91-2, 91-3, 97-1, 00-13
- ...medical and psychological aspects, 71-10
- ...passenger safety information, availability, 04-19
- ...sports parachutists, restraint systems, 98-11
- ...standards for advanced systems, 71-33
- ...wheel-well stowaways, 96-25

### **Aircraft**

- ...accident causes, 66-8, 66-25, 66-27, 66-29, 66-30, 67-23, 68-16, 69-2, 69-18, 71-9, 72-2, 73-5, 78-13, 78-31, 80-4, 82-15, 89-3, 98-5, 99-14, 99-15, 03-4, 04-4, 04-13, 04-24, 05-8, 06-7, 06-24
- ...accident investigation, 62-7, 62-9, 63-21, 63-35, 67-22, 69-18, 72-2, 73-5, 79-2, 79-6, 80-3, 80-6, 80-11, 81-10, 82-7, 83-8, 85-8, 97-21, 98-10, 99-11, 00-7, 00-22
- ...aging and maintenance, 92-3
- ...air flow and CFD prediction in a passenger cabin, 06-27
- ...attitude indicators, 73-9, 05-23
- ...aural glide slope cues for instrument approaches, 71-24
- ...biocidal fuel additive, 67-21
- ...cabin safety data bank, 79-23, 82-8
- ...cabin safety subject index, 84-1, 85-1
- ...cabin ventilation flow fields, 04-7, 06-27
- decontamination with vaporized hydrogen peroxide, 06-10
- ...cargo compartment environment, 81-11
- ...checklists, 91-7
- ...cockpit delethalization, 66-3, 66-12, 71-3, 72-6, 72-7, 72-15

- ...cockpit visual problems, 77-2, 77-7, 77-13, 77-14, 78-17, 03-12
- ...communication in light aircraft, 72-31
- ...computational fluid dynamics (CFD) in predicting pathogen distribution in a passenger cabin, 06-27
- ...contaminant distribution prediction in a passenger cabin, 06-27
- ...control forces and female pilots, 72-27, 73-23
- ...crew smoke-protective devices, 76-5, 78-4, 83-14, 89-5, 89-8, 89-11
- ...decompression hazards, 67-14, 70-12, 99-4
- ...decontamination of passenger cabin, 06-10
- ...design changes to reduce injuries, 71-3, 72-7, 83-8
- ...displays, 98-9, 98-12, 03-2, 03-5, 03-13, 04-5, 05-23
- ...ditching studies, 78-1, 91-6, 98-19, 04-12
- ...escape slides, studies of, 98-3, 99-10
- ...evacuation, 62-9, 65-7, 66-42, 70-16, 70-19, 72-30, 77-11, 78-3, 78-23, 79-5, 79-6, 80-12, 81-7, 89-5, 89-12, 92-27, 95-22, 95-25, 96-18, 98-19, 99-10, 99-30, 00-11, 01-18, 03-15, 04-2, 04-12, 05-2
- ...exits, size of in evacuation, 99-10, 04-12
- ...evacuation models, 94-11, 97-20
- ...fire, smoke protection after accidents, 67-4, 70-16, 70-20, 78-4, 83-10, 85-10, 89-5, 89-8, 89-11, 89-12
- ...fire vs. no fire on rotorcraft accidents, 05-17
- ...fires, toxicity of combustion products, 71-41, 77-9, 85-5, 86-1, 86-3, 86-5, 89-4, 91-17, 95-8
- ...flight inspection, evaluation, 95-18
- ...flight manuals, 91-7
- ...flight training devices, 94-25, 95-6
- ...floor proximity marking systems, 98-2
- ...GPS displays, 98-9, 98-12, 99-9, 99-13, 99-26, 00-4, 03-17
- ...head impact kinematics, 92-20
- ... Highway-in-the Sky (HITS) display, 00-31
- ...inspection, 89-9, 94-12, 95-14
  - -visual standards used for inspectors, 05-21
- ...instrument display, 75-12, 98-28, 00-8, 00-31
- ...interior wall padding and neck injury potential,
- ...landing, simulated night approaches, 77-12, 78-15, 79-4, 81-6
- ...life preserver retrieval, 03-9
- ...maintenance, 89-9, 90-14, 91-16, 92-3, 93-5, 93-15, 94-12, 95-14, 95-31, 96-2, 05-21
- ...medical incidents inflight, 00-13
- ...neck injury potential, 93-14
- ...NEXRAD display, 04-5
- ...noise effects measurement, 71-1, 72-32
- ...noise effects on birds, 62-4
- ...noise levels, 68-21, 68-25, 70-6

- -and pilot hearing thresholds, 05-21
- ...nongyropscopic blind flight instrument, 66-32
- ...oxygen system design, 78-9, 04-3
- ...ozone concentrations and effects, 79-20, 80-9,
- ...padding for crash protection, 66-40
- ...performance characteristics, perceived by ATCSs, 00-24, 03-8
- ...propeller paint schemes conspicuity, 78-29
- ...radioactive material shipments, 82-12
- ...readability of emergency signs in smoke, 79-22
- ...restraint installation, 66-33, 67-13, 72-15
- ...restraint system evaluation, 69-3, 69-4, 69-5, 71-12, 72-3, 72-6, 78-6, 78-12, 78-24, 79-17, 80-3, 81-10, 82-7, 94-19, 95-2, 95-30, 98-11, 99-5
- ...seat cushion flotation, 66-13, 98-19
- ...seat evaluation, 78-6, 78-24, 79-17, 80-3, 81-10, 82-7, 83-3, 90-11
- ...seat impact injuries, 66-18, 72-15, 89-3
- ...simulator operation using drugs, 64-18
- ...SST anticollision lights, 70-9, 70-15, 71-42
- ...stall warning device, 66-31
- ...standards for advanced aerospace systems, 71-33
- ...sunscreen-treated windows, 78-28
- ...toxicity of engine oil thermal degradation, 83-12
- ...unmanned aircraft, 04-24, 06-8
- ...warning signals and pilot hearing thresholds, 05-12
- ...water spray system, 98-4
- ...wheel-well passengers, 96-25

### Airport

- ...cues for approach and landing, 79-4, 79-25, 81-6, 82-6
- ...medical services, 65-3, 71-10
- ...precautionary emergency evacuation data, 99-30

# Airway facilities personnel

- ...human factors, 94-5
- ...job attitudes, 77-21, 79-11, 83-7

### Airway Science Curriculum Demonstration Project

- ...air traffic control specialists, 91-18
- ...initial evaluation, 88-5

# Airworthiness Inspectors

...assessment of job performance, 87-4

#### Alcohol

- ...alcoholic airline pilot rehabilitation, 85-12
- ...altitude effects, on blood levels, 70-5
- -on performance, 68-18, 79-26, 82-3, 85-5, 88-2
- ...ataxia test battery effects, 79-9
- ...complex performance effects, 66-29, 69-14, 72-4, 79-7, 85-5, 88-2, 94-24, 95-3, 95-7

- ...congener effects, 79-7, 79-9
- ...detection methods, 83-2, 91-12, 04-13
- ...disorientation-related responses, 71-6, 71-16, 71-20, 71-34, 71-39, 72-34
- ...findings in general aviation accidents, 66-27, 66-29, 68-16, 69-2, 78-31, 80-4, 95-28, 98-5, 04-13, 05-20
- ...hangover effects, 79-7, 79-26
- ...instrument flight performance effects, 72-4
- ...low doses and performance, 94-24, 95-3, 95-7
- ...postmortem in fatal accidents, 92-24, 98-5, 00-21, 03-18, 04-4, 04-13, 05-20
- ...problem solving effects, 72-11
- ...readiness to perform testing, 93-13, 95-24
- ...tests for alcoholism after intoxication in nonalcoholics, 83-2
- ...thalamic activity effects, 78-2
- ...visual functions effects, 78-2, 79-15

### Altitude

- ...alcohol effects, 68-18, 79-26, 82-3, 85-5, 88-2
- ...antihistamine effects on performance, 68-15
- ...antihistamine-decongestant preparations effects, 78-19, 78-20
- ...blood alcohol levels effects, 70-5
- ...blood donation effects on tolerance, 84-4
- ...chamber reactions, 77-4, 90-12
- ...civilian training need, 91-13, 03-10
- ...cosmic radiation, at SST altitudes, 71-26, 80-2
- ...cosmic radiation, crewmembers and passengers, 92-2, 00-33, 03-16, 05-14
  - -SST altitudes, 71-26, 80-2
- ...decompression hazards, 67-14, 70-12, 99-4
- ...decompression, performance after, 66-10
- ...heat effects on performance, 71-17
- ...human tolerance, 62-6
- ...marihuana effects on performance, 75-6
- ...oxygen masks, efficiency of, 62-21, 66-7, 66-9, 66-20, 67-3, 67-9, 72-10, 79-13, 80-18, 85-10, 89-10, 93-6, 98-27
- ...oxygen need, 66-28, 78-9
- ...ozone concentrations and effects, 79-20, 80-9
- ...penetrating eye injuries effects, 62-12
- ...performance effects, 66-15, 71-11, 82-3, 82-4, 82-10, 83-15, 85-3, 85-5, 88-2, 97-7, 97-9
- ...portable oxygen system, 98-27.
- ...propranolol effects on tolerance, 79-10, 80-10
- ...smokers, effects on, 97-7
- ...tolerance after crash diet, 81-2, 81-8
- ...tolerance of beta blocked hypertensives, 92-19
- ...tolerance with pulmonary disease, 77-16
- ...tolerance with sickle cell trait, 76-15, 78-30
- ...visual fields effects on glaucoma patients and the elderly, 91-1

- ...work tolerance effects, 63-33, 82-3
- ...wheel-well stowaways, 96-25

# Animal transportation

- ...freezing and subfreezing temperature effects on dogs, 87-3
- ...heat and humidity effects on dogs, 77-8, 81-11, 84-5, 87-8

# Anthropometry

- ...forensic, 79-2
- ...adult face, 78-14, 93-10
- ...adult female, 83-16
- ...air traffic controllers, 65-26
- ...center of gravity, 62-14, 65-23, 69-22
- ...faces of children for oxygen mask design, 66-9
- ...female crewmember facial anthropometry, 83-14
- ...flight attendants, 75-2, 75-13
- ...flight inspection pilots and technicians, 95-18
- ...head and face of adults, 93-10
- ...human pelvis, 82-9
- ...shoulder slope, 65-14
- ...weight distribution when sitting, 62-1

# Anthropomorphic dummies

- ...criteria for crashworthiness, 96-11
- ...design, 82-9, 83-16
- ...evaluation, 78-6, 78-24, 79-17, 83-3
- ...3- and 6-year-old dummies, 76-9
- ...thoracic mass, determination, 96-7

### **Anticollision lights**

- ...effects of backscatter, 72-8
- ...exposure effects under simulated IFR conditions, 66-39
- ...SST, 70-9, 70-15, 71-42

## **Aphakia**

- ...accident risk assessment, 95-11
- ...incidence in airmen, 91-14, 92-14

### Arousal

- ...by distracting stimuli, 71-7
- ...nystagmus effects, 62-17
- ...simulated radar control task, 75-8, 77-18, 81-12, 88-1
- ...vestibular responses effects, 63-29

#### Attention

- ...anticollision observing responses, 73-6
- ...auditory distraction effects, 72-14
- ...conspicuity of flashing and color targets, 90-3 –target blink amplitude, 97-10, 99-8
- ...personality and physiological correlates, 73-14
- ...self-estimates of distractibility, 72-25
- ...psychophysiological indices, 99-28

- ...simulated radar task, 77-18, 78-11, 79-12, 80-17, 81-12, 82-1, 82-16, 86-4, 88-1, 89-1
- ...switching in readiness to perform, 95-24
- ...time-sharing ability, 76-1, 78-33
- ...visual taskload effects on CFF change during complex monitoring, 85-13
- ...visual taskload effects on complex monitoring, 88-1, 90-3, 94-26, 95-23, 96-9, 99-28

# Audiology

- ...advanced and ATC selection, 90-13
- ...auditory fatigue, 63-19, 65-1, 65-2
- ...binaural beat perception, 63-17
- ...cockpit noise intensities, 68-21, 68-25
- ...ear-protector ratings, 73-20, 75-11
- ...earphone transient response, 63-7
- ...hearing threshold, pilots vs. non-pilots, 05-12
- ...interaural intensity difference limen, 67-10
- ...noise audiometry, 71-1
- ...noise effects on aircrew personnel, 72-32
- ...speech intelligibility improvement, 70-6, 72-31, 73-13, 76-3
- ...table of intensity increments, 66-4
- ...temporary threshold shift, 79-16

#### Automation

- ...advanced, and ATCS selection, 90-13, 92-26, 97-19, 98-23
- ...boredom and monotony as stressors, 80-1
- ...complacency on radar monitoring task, 82-1
- ...complex monitoring performance predictors, 80-17, 86-4
- ...flight progress strips, 92-31, 94-3, 95-8, 96-5
- ...general aviation, pilot responses to autopilot malfunctions, 97-24
- ...information complexity measures and design implications, 04-17
- ...physiological stress in controllers, 82-17
- ...radar performance with and without computer aiding, 89-1
- ...recovery of radar monitoring performance following startle, 83-13
- ...visual taskload effects on CFF change during complex monitoring, 85-13
- ...visual taskload effects on complex monitoring, 88-1

### Aviation maintenance

- ...human factors, 89-9, 90-14, 91-16, 92-3, 93-5, 93-15, 94-12, 95-31, 96-2
- ...visual standards and tests used for inspectors, 05-21

# Aviation medical examiners

...and drug testing program, 92-15

- ...exams of first-class certificate holders by senior AMEs, 71-38
- ...performance, 84-7

# Ballistocardiography

- ...bibliography, 65-15
- ...research and current status, 64-12
- ...stroke volume relationship, 65-8

# Behavioral types

- ...coronary-prone Type A and complex monitoring performance, 86-4
- ...Type A and ATCS training performance, 94-13

# Benzodiazepines

...analysis in forensic urine samples, 96-14

#### **Birds**

...possible sonotropic effects of a commercial air transport, 62-4

## Blood

- ...altitude effects on alcohol levels, 70-5
- ...autoregulation of renal flow, 63-32
- ...cerebrovascular disease detection, 65-4
- ...cholinesterase measurement, 67-5
- ...clot dissolution therapy, 64-5
- ...comparison of serum cholinesterase methods, 70-13, 72-12
- ...cyanide, 94-7
- ...donation effects, 84-4
- ...erythrocyte volume spectra, 63-8
- ...gene expression profiles, maintenance after blood storage, 04-1
- ...hemoconcentration with endrin poisoning, 66-11
- ...oxygen saturation, 66-7, 66-15, 66-20, 67-3, 67-9
- ...phospholipids, 71-2, 73-21, 73-22
- ...plasma catecholamine determination, 66-6, 71-15
- ...pressure changes, in ATC population, 71-19, 72-20, 78-39, 84-3
  - -in third-class certificate holders, 72-26
- ...pressure levels of active pilots, 84-3
- ...pressures by rapid indirect method, 70-21
- ...pulmonary flow with glyceryl trinitrate, 64-11
- ...pulmonary thromboembolism, 64-7
- ...sickle cell disease and trait, 76-15, 78-30, 80-20
- ...storage stability of human blood cholinesterases, 70-4
- ...tests for alcohol abuse, 83-2

### Cabin safety

- ...cabin simulator, experimental, 97-18
- ...cabin ventilation flow fields, 04-7, 06-27
  - –decontamination with vaporized hydrogen peroxide, 06-10

- ...computer evacuation models, 94-11, 97-20
- ...data bank, 79-23, 82-8
- ...passenger safety information, availability, 04-19
- ...subject index, 84-1, 85-1

# Caloric irrigation

- ...after habituation to rotation, 63-13
- ...alcohol effect on response, 71-6
- ...arousal effects on nystagmus, 62-17
- ...elicitation of secondary nystagmus, 63-3
- ...nystagmus after habituation, 63-14, 64-14, 65-19, 67-2

# Canes

...used by blind passengers, 80-12

## Carbon monoxide

- ...carboxyhemoglobin standards, 98-21
- ...cause of aircraft accidents, 68-16, 69-2, 82-15, 00-9, 05-9
- ...levels in aircraft accident victims, 70-16, 80-11,
- ...relative toxic hazards of materials, 77-9
- ...times to incapacitation of rats, 89-4, 93-7

#### Cardiovascular

- ...age and physical training effects, 63-18, 64-1
- ...antihistamine-decongestant preparations effects, 78-20
- ...ballistocardiographic research, 64-12, 65-8, 65-15
- ...blood donation effects, 84-4
- ...blood pressure measurement, 66-16, 66-36, 70-21, 84-3
- ...cerebrovascular disease detection, 65-4
- ...changes in ATC population, 71-19, 72-20, 78-39, 84-3
- ...changes in third-class certificate holders, 72-26
- ...coronary heart disease detection, 74-6, 78-38
- ...dextroamphetamine effects on heart rates, 75-14
- ...endrin effects, 63-16, 66-11
- ...evaluation with treadmill and step test, 64-3
- ...function in aviation stress protocol, 78-5
- ...glyceryl trinitrate effects on pulmonary vasculature, 64-11
- ...health, age, and performance, 64-4
- ...heart rates during instrument approaches, 70-7, 71-24, 75-12
- ...heart rates in air tanker pilots, 68-26
- ...heart rates in ATCSs, 71-2, 73-21, 73-22, 74-11
- ...heart rates in student pilots, 67-15, 69-12
- ...heart rates with complex vigilance tasks, 69-8, 75-8, 86-4
- ...heart rates with simulated sonic booms, 71-29
- ...in-flight incapacitation, 87-7

- ...physiological responses on cross-country flights, 71-23
- ...post mortem findings after accidents, 69-18, 80-8, 85-6
- ...prediction of heart rates under stress, 69-7
- ...prevalence among civil airmen, 89-2
- ...problems associated with aviation safety, 78-38
- ...recognition of posterior infarction, 64-19
- ...rehabilitation after infarction, 64-2, 66-17, 66-21
- ...responses to hyperpyrexia, 64-8
- ...rheoencephalography and cerebrovascular disease, 65-4, 67-11
- ...risk factors, 90-7
- ...startle effects on heart rates, 69-21
- ...stress effects on heart rates, 68-17
- ...thromboembolic disease treatment, 64-5
- ...transducer for heart sounds, 68-3

# Case reports

- ...ethanol origin in postmortem urine, 04-13
- ...in-flight loss of consciousness, 63-21
- ...insecticide exposure, 63-24
- ...methamphetamine involvement in a pilot fatality, 03-22
- ...physical conditioning after infarction, 66-21
- ...pulmonary thromboembolism, 64-7
- ...quinine elimination, 94-16
- ...rheoencephalography in cerebrovascular disease detection, 65-4
- ...seizures inflight, 64-6

## Center of gravity

- ...adults, 62-14
- ...children, 65-23
- ...infants, 69-22

## Certification, aeromedical

- ...airmen attrition, 72-13, 73-8
- ...alcoholic airline pilots rehabilitation, 85-12
- ...analysis of denial actions, 68-9, 74-5, 76-10,
- 78-25, 80-19, 83-5, 84-9, 85-9, 86-7, 90-5
- ...aphakia, 91-14, 92-14, 93-11, 95-11
- ...aviation medical examiner performance, 84-7
- ...color vision, tests, 67-8, 83-11, 85-7, 90-9, 93-17, 95-13, 96-22
  - -X-Chrom lens, 78-22
- ...contact lens use, 90-10, 00-18
- ...diabetic conditions, glucose concentrations in transportation accidents, 00-22
- ...disease prevalence and incidence, 73-8, 81-9, 84-8, 89-2, 90-7
- ...errors in height and weight data, 73-10
- ...estimate of active airmen, 68-5
- ...exams of first-class certificate holders by senior AMEs, 71-38

- ...gender differences in refractive surgery, 00-23
- ...glare, 94-15
- ...glaucoma, 91-1
- ...intraocular implants, 92-14, 93-11
- ...medications found in postmortem and medical history, 06-12
- ...neuropsychological screening of airmen, 92-11
- ...photorefractive keratectomy, 98-25
- ...procedures, 71-25, 82-14
- ...refractive surgery, 00-19, 00-23, 06-9
  - -gender differences, 00-23
  - -radial keratectomy, 98-25, 00-19, 06-9
  - -radial keratotomy, 99-6, 00-19, 06-9
- ...rheoencephalography and cerebrovascular disease, 65-4, 67-11
- ...sickle cell disease and trait, 76-15, 80-20
- ...suicides, aircraft-assisted in general aviation pilots, drug involvement, 06-5
- ...tests for alcohol abuse, 83-2
- ...vision restrictions and pilot demographics, 04-6
- ...vision standards and screening tests used with aircraft maintenance personnel, 05-21

# Charts

...readability, 77-13, 78-17

# Circadian periodicity

- ...bibliography of shiftwork research, 83-17
- ...disruption of intercontinental flights, 65-16, 65-28, 65-29, 65-30, 68-8, 69-17
- ...effects of shifts in wake-sleep cycle, 75-10, 76-11, 86-2
- ...excretion of magnesium and calcium, 68-4 ...rotating shiftwork, 86-2, 99-2

# Civil Aeromedical Institute (CAMI)

- ...historical vignettes, prefaces to 87-1, 97-1, 98-1, 01-1, 03-1
- ...history of aeromedical research contributions, 05-3

## Clothing

...effects on drag forces, 63-9

## Cold

- ...effect on dogs shipped by air transport, 87-3
- ...effect on manual performance, 68-13
- ...exposure after water spray, 98-4
- ...skin temperature to predict tolerance, 71-4
- ...thermal balance, 66-23
- ...thermal protection by life preservers, 85-11

# Color

- ...air traffic control displays, status of, 06-11
- ...conspicuity of radar targets, 90-3
- ...highlighting targets, 92-6

### Color vision

- ...air traffic control specialists performance, 83-11, 06-6, 06-11, 06-15, 06-22
- ...air traffic control workgroup sample, 06-2
- ...clinical tests as predictors of practical tests, 73-18, 75-1, 92-28, 92-29, 95-13, 96-22, 04-9
- ...defective, and color highlighting, 92-6
- -and radar displays, 06-22
- -and signal lights, recognition, 71-27, 71-32
- ...impairment by sunscreen materials, 78-28
- ...tests, 67-8, 85-7, 90-9, 93-17, 95-13, 96-22
- -tests used for maintenance inspectors, 05-21
- ...test illuminant, 93-16
- ...X-Chrom lens for improving, 78-22

### Communication

- ...ATC/pilot, CDTI effects, 03-13, 04-11 -voice, 93-20, 95-15, 96-26, 98-17, 98-20, 99-21, 05-19, 06-25
- ...binaural beat perception, 63-17
- ...earphone response, 63-7
- ...interaural intensity difference limen, 67-10
- ...light aircraft, 72-31
- ...organizational, and technology change, 99-25
- ...predictor for empowerment, 98-24
- ...role in aircraft maintenance and inspection, 90-10
- ...role in promoting change within Airway Facilities Service, 83-7
- ...speech intelligibility improvement, 70-6, 72-31, 73-13, 76-3
- ...table of intensity increments, 66-4
- ...tactile, 62-11, 62-16
- ...voice, methods and metrics, 96-10, 96-20, 06-25

## **Contact lenses**

- ...epidemiological study of certification, 90-10
- ...monovision and airline accident, 00-18

#### Cosmic radiation

...air carrier crew, exposure of, 80-2, 92-2, 00-33, 03-16, 05-14

# Crashworthiness

- ...dummy criteria, 96-11
- ...energy-absorbing seat effectiveness, 83-3, 90-11
- ...head impact and interior walls, 92-20, 93-14
- ...occupant survival in general aviation accidents, 81-10, 82-7, 83-8, 98-3

# Deceleration

- ...bibliography, 63-30
- ...cockpit delethalization, 66-3, 66-12, 72-6, 72-7, 72-15, 81-10
- ...head impacts while wearing restraint systems, 72-6

- ...human tolerance, 62-6, 83-3
- ...illumination effects during angular deceleration,
- ...impact injuries in pregnancy, 68-6, 68-24
- ...kinematics of human body, 62-13
- ...padding for crash protection, 66-40
- ...rearward-facing seats, 69-13
- ...restraint systems, 67-13, 69-3, 69-4, 69-5, 69-13, 72-3, 72-15, 80-3, 81-10, 82-7, 83-8, 99-5
- ...seat impact injuries, 66-18, 72-15, 81-10, 82-7
- ...side-facing seats, 69-13
- ...survival of extreme vertical impacts, 62-19
- ...survival of free-fall impacts, 63-15
- ...survival of water impacts, 65-12
- ...tolerances of face, 65-20

# **Decision-making**

- ...employee participation in, 91-10, 92-13, 92-17
- ... "expert" pilot model, 97-6
- ...perceptions of aircraft performance characteristics by ATCSs, 00-24
- ...personal minimums tool, 96-19, 98-6
- ...skills in pilots, 98-7
- ...training in pilots, 87-6, 96-19, 98-6
- ...weather information, use of, 97-3, 97-23, 04-5
- ...willingness to take off into marginal weather, 05-7, 05-15

# Decompression

- ...altitude chamber experience, 77-4, 90-12
- ...effects on performance, 66-10
- ...effects of propranolol on TUF, 79-10, 80-10
- ...need for civilian training, 91-13, 03-10
- ...oxygen mask evaluation, 66-20, 67-3, 72-10, 79-13, 80-18, 96-4, 98-27, 00-6
- ...pressurized small aircraft, 67-14
- ...supersonic transports, 99-4
- ...tolerable profiles for SST, 70-12

## Depth perception

- ...general, 62-15, 63-10, 63-20, 63-28, 64-13, 65-11, 65-32, 66-22, 66-24, 67-18, 67-20
- ...light adaptation device, 66-38
- ...monovision contact lenses in airline accident, 00 - 18

## Diet

- ...human tolerance, effects, 81-2
- ...performance, effects, 81-8

### Disorientation

- ...accidents due to, 78-13, 95-1, 96-21
- ...adaptation, 65-18, 65-24, 66-37, 67-2, 67-6, 67-7, 67-12, 67-19, 68-2, 68-28, 69-20, 74-3

- ...alcohol effects, 71-6, 71-16, 71-20, 71-34, 71-39, 72-34
- ...familiarization techniques, 70-17, 77-24
- ...visually induced, 69-23, 70-2, 71-22

### Distraction

- ...auditory distraction and performance, 72-14
- ...susceptibility, measurement of, 72-25

# Ditching

- ...flotation and survival equipment studies, 78-1, 85-11, 03-9, 04-12
- ...frequency of occurrence, 98-19
- ...infant flotation device, 71-37, 91-6
- ...seat cushion flotation, 66-13, 95-20
- ...water survival training programs, 98-19

## **DNA**

- ...detection of postmortem alcohol-producing microorganisms, 00-16
- ...identification of forensic specimens, 06-14
- ...profiling for quality assurance, 98-18, 99-14

# Drugs

- ...aircraft accidents, role of, 68-16, 78-31, 85-8,
  - 92-23, 94-14, 95-28, 96-14, 97-14, 98-10, 98-18,
  - 99-29, 00-20, 00-21, 03-7, 05-20 –quality assurance of forensic findings, 99-11, 99-15, 04-15
- ...antihistamine effects, at altitude, 68-15, 78-19, 78-20
  - -on cognitive performance, 99-20
  - –on shiftwork performance, 97-25
- ...antimotion sickness, 81-16, 82-19
- ...atropine, and performance, 93-19
  - -and Phosdrin effects on vision, 73-4
- ...benzodiazepines, forensic analysis, 96-14
- ...butalbital, forensic analysis, 00-29
- ...cocaine, forensic analysis, 03-23, 03-24
- ...chlordimeform toxicity, 77-19
- ...chlorpheniramine, forensic analysis, 99-29
- ...complex performance effects, 69-9
- ...detection and identification, 92-25, 96-17, 97-14, 98-18, 04-15, 05-8, 05-10, 05-11, 05-20, 06-3, 06-12, 06-17
- ...dextroamphetamine, effects during angular acceleration, 73-17, 76-12
  - -effects during sleep loss, 75-14
- ...enantiomeric analysis of ephedrines and norephedrines, 05-8
- ...fatigue, and use, 63-12, 75-14
- ...glyceryl trinitrate effects on pulmonary vasculature,
- ...lithium carbonate effects on performance, 77-17 ...marihuana, 73-12, 85-8

- ...marihuana and altitude effects on performance, 75-6
- ...melatonin, 98-10
- ...methamidophos poisoning, 78-26
- ...methamphetamine, forensic finding, 03-22
- ...opiate determination (vs. poppy seed use) in post-mortem sample, 05-11
- ...orthostatic tolerance effects, 63-34
- ...performance effects in aircraft simulator, 64-18
- ...post-mortem findings and medical history, 06-12
- ...propranolol, effects on altitude tolerance, 79-10,
  - -quantitation, 05-10
- ...readiness to perform testing, 93-13
- ...secobarbital effects during angular acceleration, 73-17
- ...selegiline metabolites, 97-14
- ...sildenafil (Viagra), method for detecting in postmortem samples, 00-20, 06-3
- ...testing programs and AMEs, 92-15
- ...tranquilizer, effects on body temperature, 63-23, 66-14
  - -use in flight training, 69-12
- ...triamterene in fatal accident, 92-13
- ...Vardenafil (Levitra), method for detecting in post-mortem samples, 06-17
- ...visual reflexes effects, 79-15
- ...work capacity effects, 63-34

## **Earphones**

- ...headset interference tones, 92-4
- ...transient response, 63-7

### Earplugs

...ratings, 73-20, 75-11

### Education

- ...aviation medical examiners, 84-7
- ...factor, in air traffic controller selection, 76-6, 96-6 -in air traffic controller success, 76-6, 83-6

### Electrocardiogram

- ...amplitude/frequency analysis, 74-6
- ...diagnosis of posterior infarction, 64-19

## Energy

- ...cost of treadmill work, 62-5
- ...energy-absorbing seat effectiveness, 83-3, 90-11

#### **Environment**

- ...aerospace, commercial passengers, medical screening guidance, 06-1
- ...cabin ventilation, flow fields, 04-7
- -computational fluid dynamics for predictions, 06-27

- -decontamination with vaporized hydrogen peroxide, 06-10
- ...cargo compartments, 81-11
- ...effects of mass air transportation, 71-10

## Equipment

- ...air traffic control displays and color vision, 06-2, 06-6, 06-11, 06-15, 06-22
- ...air traffic situation assessment (SATORI), 93-12
- ...alcohol detection, 91-12
- ...anthropometry in design, 65-26, 75-2
- ...anticollision lights, 66-39, 70-9, 70-15, 71-42, 72-8
- ...ARTS-III effects on controller stress, 76-13
- ...attitude indicators, equivalence tests, 05-23
- ...automation design, measures of information complexity, 04-17
- ...blood pressure measurement, 66-16, 70-21
- ...Cockpit Display of Traffic Information (CDTI), 00-30, 03-2, 03-5, 03-13, 04-11, 04-20
- ...compact instrument display, 75-12
- ...crew smoke-protective devices, 76-5, 78-4, 78-41, 83-14, 89-8, 89-11, 05-18
- ...disorientation familiarization, 70-17
- ...Emergency Escape Breathing Device, 92-18
- ...emergency lighting, 66-42, 79-22, 80-13, 81-7
- ...escape slides, strength, 98-3
- ...evaporative water loss, 67-17
- ...fire, smoke protection, 67-4, 70-20, 78-4, 83-10, 85-10, 89-5, 89-8, 89-11, 89-12, 05-18
- ...flotation and survival, 78-1, 85-11
- ...GPS displays, 98-8, 98-12, 99-9, 99-13, 99-26, 00-4, 03-17
- ...head injury criteria (HIC) test component test device, evaluation, 04-18
- ...head-up displays, 98-28
- ...Highway-in-the-Sky (HITS) display, 00-31
- ...infant flotation device, 71-37, 91-6
- ...instrument readability by senior pilots, 77-2, 77-7
- ...lapbelt restraint in pregnancy, 68-24
- ...life preserver retrieval, 03-9
- ...light adaptation device, 66-38
- ...medical kits, 91-2, 91-3, 00-13, 00-13
- ...NEXRAD display, 04-5
- ...nongyroscopic blind flight instrument, 66-32
- ...oxygen, 62-21, 66-7, 66-9, 66-10, 66-20, 67-3, 67-9, 72-10, 78-4, 79-13, 80-18, 83-10, 85-10, 89-5, 89-10, 93-6, 95-17, 96-4, 98-27, 00-6, 04-3
- ...padding for crash protection, 66-40
- ...performance testing, 66-19
- ...personnel lifting devices, rotorcraft, 98-13
- ...protective, for aircraft accidents, 65-7, 66-3, 66-12
- ...restraint systems, 67-13, 69-3, 69-4, 69-5, 72-3, 72-6, 83-8, 94-19, 99-5

- ...seat cushion flotation, 66-13
- ...secondary container alternative for transportation of infectious substances, 95-29
- ...stall warning, 66-31
- ...transducer, 68-3
- ...upper torso restraint acceptance, 71-12
- ...visual displays, methods to assess complexity in air traffic control, 05-4

### Evacuation, passenger emergency

- ...acoustic signals for exit location, 79-5
- ...air carrier accidents, 62-9, 65-7, 70-16
- ...bibliography, 63-30
- ...blind passengers, 80-12
- ...cabin simulator, experimental, 97-18
- ...children, 66-42, 01-18
- ...computer models, 94-11
- ...ditching (evacuation into water), simulated, 04-12
- ...Emergency Escape Breathing Device, 92-18
- ...emergency lighting, aisle seat arm rests, 81-7
  - -exit signs, 79-22, 80-13, 81-7
  - -floor, 98-2
- ...escape slides and platforms, 96-18, 98-3
- ...handicapped passengers, 77-11
- ...history of smoke/fume protective breathing equipment, 87-5
- ...human external loads, 98-13
- ...infants, 66-42, 01-18, 05-2
- ...injuries, 79-6, 79-23, 82-8, 99-30, 03-15
- ...motivation of passengers, 96-18, 04-2
- ...passenger flow rates between compartments, 78-3
- ...passenger safety information, availability, 04-19
- ...passenger workload and protective breathing, 87-2, 89-5
- ...precautionary, 99-30, 00-11
- ...railroad accident, 73-1
- ...readability of emergency signs in smoke, 79-22, 80-13, 81-7
- ...seating configuration, 89-14, 92-27, 95-22, 03-15
- ...simulation by computer models, 72-30, 78-23, 94-11, 97-20
  - -experimental cabin, 97-18
- ...SST mockup tests, 70-19
- ...size of exits in evacuation, 99-10, 04-12
- ...tests using L-1649, 66-42
- ...tests using protective smoke hood, 70-20, 89-12, 05-18
- ...type III exits, 92-27,95-22, 95-25, 03-15, 04-2
- ...water survival training programs analysis, 98-19

# Exercise

- ...ausculatory and intra-aortic pressures, 66-36
- ...human tolerances, effects on, 82-4, 82-10
- ...magnesium and calcium excretion, effects on, 68-4

- ...myocardial infarction, before and after, 64-2 –effects after, 66-17, 66-21
- ...tolerance at altitude, 63-33
- ...treadmill work, energy cost of, 62-5
- ...air traffic controller selection, 63-31, 74-8, 78-7, 83-6
- ...ATCS, correlation with age and performance, 67-1, 73-7
- ...pilots in general aviation accidents, 77-10
- ...relation to reported symptoms of ATCSs, 65-6

## Eye

- ...age and binocular fusion time, 66-35
- ...airman visual acuity, midair collisions, 75-5
- ...alcohol effects on eye movements, 72-34
- ...anticollision lights, 66-39, 70-9, 70-15, 71-42, 72-8
- ...aphakia, prevalence in civil airmen, 91-14, 92-14, 93-11
- ...bifocal effects on radar monitoring, 82-16
- ...bright lights and visual disturbances during nighttime flight operations, 06-28
- ...contact lenses, 90-10, 00-18
- ...cockpit visual problems of senior pilots, 77-2, 77-7, 77-13, 77-14, 78-17
- ...color vision and signal lights, 71-27, 71-32, 73-18, 75-1, 78-22, 93-17, 04-14, 06-2
- ...color vision tests, for ATCS, 83-11, 85-7, 90-9, 92-28, 92-29, 95-13, 96-22, 04-10, 04-14
  - -for aviation maintenance inspectors, 05-21
- ...depth perception, 63-10, 63-28, 67-20, 00-18
- ...equidistance tendency, 65-11
- ...fatigue effects on binocular fusion time, 69-1
- ...glare tests, 94-15
- ...glaucoma, visual field and altitude, 91-1
- ...laser light illumination, effects on simulator performance, 03-12, 04-9
  - -incidence during flights, 06-23
- ...lateral movements in student pilots, 67-15
- ...movements during simulated air traffic control, 94-26, 95-23, 96-9
- ...neural control of ciliary muscle, 63-5
- ...occupational vision, en route centers, 96-12, 96-27
- ...optokinetic stimulation, 70-2, 70-10, 71-22
- ...pathology in accident airmen, 81-14, 83-18
- ...penetrating injuries, 62-12
- ...photic stimulation, 66-39
- ...photorefractive keratectomy, 98-25
- ...pilot demographics and vision restrictions, 04-6
- ...propeller paint schemes conspicuity, 78-29
- ...pupillary movement with fatigue, 65-9
- ...pupillary reflex with age, 65-25
- ...radial keratectomy, 98-25, 00-19, 06-9
- ...radial keratotomy, 99-6, 00-19, 06-9

- ...reaction time, flash luminance and duration, 67-24
- ...refractive surgery and aeromedical certification, 00-19, 06-9
- ...senior pilots, cockpit visual problems, 77-2, 77-7, 77-13, 77-14, 78-17
- ...simulation of objects moving in depth, 65-32
- ...size and distance perception, 62-15, 64-13, 66-22, 66-24, 67-18
- ...spatial extent, perception of, 63-20
- ...spiral aftereffect test, 64-9, 64-10, 64-17, 68-10, 69-15, 71-31
- ...target detection, highlighted, 97-10, 99-8
- ...tests for color vision, 67-8, 83-11, 93-16, 93-17, 06-2
  - -tests for aviation maintenance inspectors, 05-21
- ...two-flash thresholds, 68-20, 70-15, 71-42
- ...vision through sunscreen materials, 78-28
- ...visually induced disorientation, 69-23, 70-2, 71-22
- ...X-Chrom lens for improving color vision, 78-22

# Fatigue

- ...air tanker pilots, 68-26
- ...antihistamine-decongestant preparations effects, 78-20
- ...auditory, 63-19, 65-1, 65-2
- ...aviation activities, 65-13, 81-13
- ...binocular fusion time effects, 69-1
- ...Composite Mood Adjective Check Lists to measure in ATCSs, 71-21
- ...8- vs. 10-hr. work schedules, 95-32
- ...eye blink-rate measures, 94-17, 94-26, 99-28
- ...intercontinental jet flights, 65-16, 65-28, 65-29, 65-30, 68-8, 69-17
- ...mitigation with Spartase, 63-12
- ...plasma catecholamine determination, 66-6, 71-15
- ...pupillary movement with, 65-9
- ...readiness to perform testing, 93-13, 95-24
- ...shiftwork, rotating, 86-2, 99-2
  - -effects on commuting risk factors before and after shift, 06-13
  - -effects on wake-sleep cycle, 75-10, 76-11, 85-2, 95-12, 95-19
- ...sleep deprivation effects, 70-8, 75-14, 85-3
- ...tolerance after crash diet, 81-2
- ...tolerance after exercise, 82-4, 82-10
- ...visual, during vigilance task, 94-26, 96-9
- ...visual taskload effects on CFF change during complex monitoring, 85-13

## **Federal Air Surgeon**

- ...review of 1966 program, 67-25
- ...review of 1976 program, 76-8

#### Fire

- ...crew smoke-protective devices, 76-5, 78-4, 78-14, 78-41, 83-14, 05-18
- ...effects in air carrier accidents, 62-9, 65-7, 70-16
- ...flammability of toiletries in oxygen, 63-27
- ...passenger protective breathing devices, 67-4, 70-20, 83-10, 85-10, 87-2, 87-5, 89-5, 89-8, 89-11, 89-12, 05-18
- ...smoke effects on identifying emergency signs, 79-22, 80-13, 81-7
- ...toxicity of products in aircraft fires, 7 1-41, 77-9, 85-5, 86-1, 86-3, 86-5, 89-4, 90-15, 90-16
- ...toxicity of seat fire-blocking materials, 86-1
- ...vs. non-fire, forensics, 00-9, 05-9 -in rotorcraft accidents, 05-17

# Flight attendants

- ...anthropometry, 75-2
- ...functional strength, 75-13
- ...injuries, cabin safety data bank, 79-23, 82-8
- ...ozone effects, 79-20
- ...water survival training programs, 98-19

### Flotation devices

- ...infant, 91-6
- ...life preserver retrieval, 03-9
- ...methods of seat cushion use, 95-20
- ...personal devices, 98-19

## Forensics (See Toxicology)

#### **Fuel**

...biocidal additive, 67-21

#### G forces

- ...aerobatics effects, 72-28, 82-13
- ...simulation with lower body pressure box, 79-8, 82-3, 82-4
- ...tolerance after crash diet, 81-2
- ...tolerance effects of antihistamine-decongestant preparations, 78-20

## Galactic cosmic radiation

...effect on air carrier crewmembers, 80-2, 92-2, 00-33, 03-16, 05-14

# Global positioning system (GPS)

- ...design considerations, 98-9, 98-12, 99-13, 99-26, 00-4
- ...effectiveness, 03-17

# Handicapped persons

- ...blind passengers, 80-12
- ...pilot positions in radar training, 80-5

### Heat

- ...altitude effects on performance, 71-17
- ...complex performance effects, 69-10, 72-17
- ...dogs shipped by air transport, 77-8, 81-11, 84-5, 87-8
- ...human tolerances, 70-22, 71-4
- ...maintenance of thermal balance, 66-23
- ...manual performance effects, 68-13
- ...measurement of evaporative water loss, 63-25
- ...tolerance limits for rats and mice, 86-8
- ...tranquilizer effects on loss and conservation, 63-23, 66-14

# Hearing

- ...acoustic signals for emergency evacuation, 79-5
- ...auditory fatigue, 63-19, 65-1, 65-2
- ...binaural beat perception, 63-17
- ...cockpit noise intensities, 68-21, 68-25
- ...conservation with earplugs, 73-20, 75-11
- ...earphone transient response, 63-7
- ...engine noise effects, pilots vs. non-pilots, 05-12
- ...headset interference tones, 92-4
- ...interaural intensity difference limen, 67-10
- ...noise audiometry, 71-1
- ...noise effects on aircrew personnel, 72-32
- ...pilots vs. non-pilots, 95-12
- ...speech intelligibility improvement, 70-6, 72-31, 73-13, 76-3
- ...table of intensity increments, 66-4
- ...temporary threshold shift, 79-16, 92-4

## Hijacking

...deterrence, 78-35

# History (CARI/CAMI)

- ...historical vignettes, prefaces to 87-1, 97-1, 98-1, 01-1, 03-1, 05-1
- ...history of aeromedical research contributions, 05-3

### Human

- ...adult female anthropometry, 83-16
- ...angle of shoulder slope, 65-14
- ...body center of gravity, 62-14
- ...body kinematics on deceleration, 62-13
- ...center of gravity, 62-14, 65-23, 69-22
- ...child body models, 76-9
- ...DNA profiling, 98-18
- ...head injury criteria (HIC) component test device, evaluation, 04-18
- ...mass distribution of children, 76-9
- ...pelvis spatial geometry, 82-9
- ...physical fitness testing, 63-6
- ...responses to hyperpyrexia, 64-8
- ...survivability of free-fall impacts, 63-15, 65-12, 68-19

- ...thorax, determination of effective mass, 96-7
- ...tolerances, 62-6, 71-3, 71-4, 71-13, 81-2, 82-3, 82-4, 82-10
- ...tolerances to facial impact, 65-20, 66-12, 66-40 ...tolerances to heat, 70-22, 71-4

### Human factors (also see: Performance)

- ...accident reporting system Human Factors Analysis and Classification System, 00-7, 00-28, 01-3, 03-4, 05-24, 05-25, 06-7, 06-24
- ...air traffic control operational errors/deviations, role of shiftwork and fatigue, 99-2
  - -development of temporal markers to profile, 06-20
  - -review of human factors literature, 06-21
  - -role of age, 05-22
  - -severity index, 05-5
  - -evaluation of HFACS and other models to describe causes 05-25
- -strategies for reducing causal factors, 03-19, 06-20 ...air traffic sector complexity, 00-24, 03-8, 05-16, 06-29
  - -and operational errors, 98-14, 06-4
- ...Air Traffic Selection and Training (AT-SAT) simulation, 00-2, 00-12
- ...assessment of complex performance, 69-6, 69-16
- ...attitude indicators, equivalence tests, 05-23
- ...auditory startle responses, 88-4
- ...aviation maintenance, 89-9, 90-14, 91-16, 92-3, 93-5, 93-15, 94-12, 95-14, 95-31, 96-2, 05-21
- ...aviation safety, 63-35, 66-8, 66-25, 66-27, 70-18, 71-9, 71-10, 72-2, 73-5, 80-6, 92-3, 94-5, 94-27, 99-7, 00-7, 00-28, 01-3, 03-4 04-24, 05-7, 05-15, 05-24, 05-25, 06-7, 06-8, 06-18, 06-26
- ...CDTI/ADS-B operational evaluation, 00-30, 03-2, 03-5, 03-13, 04-11, 04-20
- ...color displays and color defect, 06-2, 06-6, 06-11, 06-15, 06-22
- ...crew resource management, FAA aircrews, 96-24
- ...decision making, preflight, 96-19, 97-3, 97-23, 98-7, 05-7, 05-15
- ...emergency evacuation, 65-7, 70-16, 95-25, 96-18, 94-11, 97-20, 98-19, 99-10, 99-30, 03-15
  - FAIT analysis, applied to traffic awareness in free-flight, 03-5
- ...flight-control problems in unmanned aircraft accident, 06-8
- ...flight progress strips, 95-4, 95-9, 96-5, 98-26, 00-5
- ...flight simulator research, 96-15, 96-16, 97-9, 97-24, 98-12, 98-28, 04-20
- ...GPS use, 98-9, 98-12, 99-9, 99-13, 99-26, 00-4, 03-17
- ...hearing thresholds of pilots and cockpit warning signals, 05-12

- ...Human Factors Analysis and Classification System (HFACS), 00-7, 00-28, 01-3, 03-4, 05-24, 06-24
- ...human factors review of operational error literature, 06-21
- ...intervention strategies for aircraft accident prevention , 06-24
- ...JANUS technique applied to ATC operational errors, 03-21, 06-21
- ...job task taxonomy, 93-1, 95-16
- ...NEXRAD display use, 04-5
- ...operational demonstration of flight inspection aircraft, 95-18
- ...photic stimulation responses, 66-39
- ...rotorcraft personnel lifting devices, 98-13
- ...SATORI, 93-12, 97-13, 98-14
- ...severe weather flying, 66-41, 05-15
- ...situation awareness and performance in air traffic control, 99-3
- ...target blink amplitude, attention-getting value, 97-10, 99-8
- ...unmanned aircraft, accident/incident data, 04-24 –flight-control problems, 06-8
- ...workstation design, flight inspection aircraft, 95-18
- ...visual displays, methods to assess information and cognitive complexities, 05-4
- ...WinMine analytic tool applied to accident data, 06-26

# Hypothermia

- ...passengers, 94-10, 95-20
- ...wheel-well stowaways, 96-25

### Hypoxia

- ...and beta-blocked hypertensives, 92-19
- ...blood donation effects, 84-4
- ...civilian training need, 91-13, 03-10
- ...human tolerance, 62-6, 63-33
- ...interaction with marihuana, 75-6
- ...oxygen need, 66-28, 04-3
- ...performance decrement, 66-10, 66-15, 71-11, 71-17, 97-9
- ...propranolol effects, 79-10, 80-10
- ...sickle cell trait susceptibility, 76-15, 78-30, 80-20
- ...supersonic transport, decompression in, 99-4
- ...visual field and glaucoma, 91-1
- ...wheel-well stowaways, 96-25

### Identification

- ...DNA, profiling of accident victims, 98-18, 99-14
  —identification of forensic postmortem specimens,
  06-14
- ...enantiomeric compositions of compounds in cold remedies, 05-8
- ...sex and race diagnosis from cranial measurements, 79-2

## In-flight health care

- ...medical emergencies, 97-2, 00-13
- ...medical kits, 91-2, 91-3, 97-2, 00-13

#### Illusions

- ...spiral aftereffect, 64-9, 64-10, 64-17, 68-10, 69-15, 71-31
- ...visual, 70-2, 71-22, 77-12

## **Injuries**

- ...agricultural aircraft accidents, 72-15, 80-3
- ...analysis in railroad accident, 73-1
- ...brain tolerances to concussion, 71-13, 74-4
- ...cabin safety data bank, 79-23, 82-8
- ...cockpit delethalization, 66-3, 66-12, 71-3, 72-7, 81-10, 82-7
- ...correlation with kinematic behavior, 62-13
- ...criteria for aircraft crashworthiness, 96-11
- ...decompression of small aircraft, 67-14
- ...emergency and precautionary evacuations, 79-6, 79-23, 82-8, 99-30, 00-11, 03-15
- ...eye, 62-12
- ...facial tolerances to impacts, 65-20
- ...head impacts while wearing restraint systems, 72-6, 92-20
- ...head injury criteria (HIC) component test device, evaluation, 04-18
- ...impact in pregnancy, 68-6, 68-24
- ...in free falls, 63-15
- ...neck, 93-14
- ...padding for crash protection, 66-40
- ...precautionary evacuations, 99-30
- ...prevention in aircraft accidents, 71-3, 94-19
- ...produced by restraint systems, 69-5, 89-3
- ...rearward-facing seats, 62-7, 69-13
- ...restraint systems to prevent, 67-13, 69-3, 69-4, 69-5, 69-13, 72-3, 82-7, 83-8, 98-11
- ...seat impacts, 66-18
- ...side-facing seats, 69-13
- ...smoke and fire, 62-9, 70-16
- ...vertical crash forces, 62-1
- ...vertical impact in seated position, 62-19
- ...water impacts, 65-12, 68-19

# Instruments

- ...attitude indicators, 73-9, 05-23
- ...automation design, measures of information complexity, 04-17
- ...cockpit displays of traffic information (CDTI), 00-30, 03-2, 03-5, 03-13, 04-11, 04-20
- ...compact display, effects on performance, 75-12
- ...GPS, design considerations, 98-9, 98-12, 99-26, 00-4
  - -effectiveness, 03-17

- ...head-up displays, 98-28
- ...Highway-in-the Sky (HITS) displays, 00-31
- ...NEXRAD weather display, 04-5
- ...information priorities, 00-26
- ...navigational display formats, 96-16, 00-8, 04-20
- ...radiation detection, 71-26
- ...readability by senior pilots, 77-2, 77-7

## Job attitudes

- ...air traffic controllers, 74-7, 74-12, 75-3, 79-11, 91-10, 00-17, 04-23
- ...Airway Facilities Service, 77-21, 79-11, 83-7
- ...aviation business operators, 87-4
- ...burnout, 92-7
- ...diversity training, 95-10
- ...empowerment, perceptions of, 98-24
- ...exchange ideology, 91-11
- ...FAA survey 2000, process feedback, 03-11
- ...FAA survey 2003, agency-wide work attitudes, 04-22
  - -Air Traffic Organization work attitudes, 04-23
- -analysis of employee comments, 05-13
- ...gender, equity, and satisfaction, 92-9
- ...goal congruence, 92-8
- ...intent to leave job, 91-15, 06-30
- ...neuropsychological screening of airmen, 92-11
- ...organizational change, and cynicism, 99-27, 00-14
- ...organizational communications, and trust, 99-25
- ...organizational politics, perceptions of, 92-10
- ...participation in decision-making, 92-17
- ...safety behavior, 97-8
- ...safety perceptions, 99-19
- ...turnover, and intent to leave job, 91-15, 06-30

### Judgment

- ...decision-making in pilots, 97-3, 97-23, 98-7
- ...training in pilots, 87-6, 98-6

## Kidney

- ...autoregulation mechanism, 63-32
- ...effects of acute arterial occlusion, 63-22, 65-27
- ...effects of increased venous pressure, 62-18, 63-1
- ...effects of pesticides, 63-26, 66-11

# Lighting

- ...cabin, 79-22, 80-13, 81-7, 98-2
- ...cockpit, 77-2, 77-13, 77-14, 78-17

## Management

- ...crew resource, FAA flight crews, 96-24
- ...empowerment, predictors of perceived, 98-24
- ...ergonometric interventions to reduce worker stress, 99-17
- ...FAA employee attitude survey, year 2000, process feedback, 03-11

- -year 2003 agency-wide work attitudes, 04-22
- -year 2003 Air Traffic Organization work attitudes, 04-23
- -year 2003 analysis of employer comments, 05-12
- ...health awareness, survey of FAA programs, 00-3
- ...job task analysis for supervisors, 91-5
- ...matrix teams, commitment, 93-18
- ...organizational change, and cynicism, 99-27, 00-14
- ...organizational commitment, 92-21
- ...organizational communication, and technology change, 99-25
- ...training effectiveness, 75-9, 78-32
- ...training needs, 90-2
- ...turnover and intent to leave job, 91-15, 06-30
- ...workplace safety behaviors, influence on, 97-8 –employee safety perceptions, 99-19

#### Medical kits

...used in flight, 91-2, 91-3, 97-2, 00-13

### Motion sickness

- ...susceptibility, 76-14
- ...treatment effects, 81-16, 82-19

### Motivation

- ...airway facilities personnel, 77-21
- ...factors in ATC work, 71-30, 74-12
- ...passengers, in aircraft evacuations, 96-18, 03-15, 04-2

## Neurology

- ...alcohol effects on ataxia test battery, 79-9
- ...alcohol effects on visual functions, 78-2, 79-15
- ...brain tolerances to concussion, 71-13, 74-4
- ...central factor in auditory fatigue, 63-19
- ...chlordimeform toxicity, 77-19
- ...conditions associated with aviation safety, 81-3
- ...drug effects on performance, 64-18
- ...endrin effects, 63-16, 70-11
- ...in-flight vertigo and unconsciousness, 63-21
- ...neuropsychological test battery, 92-11, 95-7
- ...nucleus rotundus, 77-22
- ...organophosphate insecticide effects, 63-24, 72-29, 73-3, 73-4, 79-15
- ...photic stimulation, 66-38
- ...pupillary movement, 65-9, 65-25
- ...rheoencephalography in cerebrovascular disease detection, 65-4, 67-11
- ...seizures in flight, 64-6
- ...spiral aftereffect test, 64-9, 64-10, 64-17, 68-10, 69-15, 71-31
- ...studies at GCRI, 64-1
- ...vestibular tests, 75-4

#### Noise

- ...aircrew personnel effects, 72-32
- ...auditory fatigue, 63-19, 65-1, 65-2
- ...birds, effects on, 62-4
- ...ear-protector ratings, 73-20, 75-11
- ...engine, and pilot vs. non-pilot hearing thresholds, 05-12
- ...intensity in aircraft cockpits, 68-21, 68-25, 95-18
- ...performance effects of simulated radar task, 79-24, 83-13
- ...performance impairment, 72-14
- ...simulated sonic boom effects, 71-29, 72-19, 72-24, 72-35, 73-16, 74-9
- ...sonic boom startle effects in field study, 73-11
- ...speech intelligibility improvement, 70-6, 72-31, 73-13, 76-3
- ...temporary threshold shift, 79-16

## Nystagmus

- ...adaptation effects, 66-37, 67-6, 67-7, 67-12, 67-19, 69-20
- ...alcohol effects, 71-6, 71-16, 71-20, 71-34, 71-39, 72-34
- ...antimotion sickness drug effects, 81-16
- ...arousal effects, 62-17, 63-29
- ...caloric habituation, 63-14, 64-14, 65-18, 67-2
- ...dextroamphetamine and secobarbital effects, 73-17
- ...habituation to rotation, 63-13, 65-24, 68-2
- ...illumination effects during angular deceleration, 68-28
- ...optokinetic stimulation, 70-2, 70-10, 71-22
- ...secondary, elicitation by irrigation, 63-3
- ...sleep deprivation, during, 86-9
- ...translations of reports, Tech. Pub. #1, 64-16, 65-17, 66-2
- ...vertical, 68-2

### Orthostatic tolerance

- ...alcohol effects at altitude, 82-3
- ...and beta blocked hypertensives, 92-19
- ...physical exertion effects, 82-4

## Oxygen

- ...equipment studies, 79-13, 80-18, 89-10, 92-18, 92-22, 95-17, 98-27, 00-6, 04-3, 05-18
- ...flammability of toiletries, 63-27
- ...need at altitude, 66-28, 97-9
- ...need for training among civilians, 91-13, 03-10
- ...system design, 78-9

## Oxygen masks

...crew smoke-protective devices, 76-5, 78-4, 78-14, 78-41, 83-14, 89-8, 89-11, 05-18

- ...design for children, 66-9
- ...disposable, 66-7
- ...donning time after decompression, 66-10
- ...evaluation, 62-21, 66-7, 66-20, 67-3, 67-9, 72-10, 78-4, 79-13, 80-18, 83-10, 85-10, 87-5, 89-5, 93-6, 96-4, 98-27, 00-6, 04-3, 05-18

## Ozone

- ...chronic effects, 80-16
- ...effects under simulated flight conditions, 79-20, 80-9
- ...review of effects, 89-13

## **Passengers**

- ...aerospace, commercial, guidance for medical screening, 06-1
- ...blind, cane use in emergency evacuation, 80-12
- ...child restraints, 94-19, 95-30
- ...cold/wet exposure, 94-10, 98-4
- ...commercial aerospace, guidance for medical screening, 06-1
- ...emergency evacuation, computer model, 72-30, 78-23, 94-11, 97-20
  - -experimental cabin, 97-18, 03-15, 04-2
  - -infants, 01-18, 05-2
  - -precautionary, 99-30, 00-11
  - -seating configurations, 89-14, 03-15
  - -size of exits, 99-10
- ...emergency lighting, floor, 98-2
- ...flow rates between compartments, 78-3
- ...handicapped emergency evacuation, 77-11, 80-12
- ...head injury analysis, 92-20
- ...human external loads, rotorcraft, 98-13
- ...illness and injuries, cabin safety data bank, 79-23
- ...injuries, during emergency evacuation, 79-6, 79-23, 03-15
  - -during precautionary evacuation, 99-30
- ...medical kits, use of, 91-2, 91-3
- ...neck injury analysis, 93-14
- ...oxygen masks, 79-13, 80-18, 95-17, 96-4
- ...ozone effects, 80-9, 89-13
- ...protective breathing devices, 67-4, 70-20, 83-10, 85-10, 87-2, 87-5, 89-5, 05-18
- ...safety information, availability, 04-19
- ...sport parachutists, 98-11
- ...water spray exposure, 98-4
- ...wheel-well stowaways, 96-25

## **Patients**

- ...air transport with eye injuries, 62-12
- ...civilian air ambulance services, 71-18, 82-5
- ...human external loads, 98-13
- ...supplemental oxygen from Molecular Sieve oxygen concentrators, 92-22

# Perception

- ...anticollision lights, 66-39, 70-9, 70-15, 71-42
- ...approach angle in simulated night landings, 81-6, 82-6
- ...auditory fatigue, 63-19
- ...binaural beat, 63-17
- ...Broca-Sulzer phenomenon, 68-27
- ...color, 67-8, 83-11, 90-9, 06-2, 06-6, 06-11, 06-15, 06-22
- ...depth, 63-10, 63-28, 65-11, 65-32, 67-20, 00-18
- ...highlighted targets on displays, 97-10, 99-8
- ...induced decrements, 93-19
- ...interaural intensity difference limen, 67-10
- ...matching loudness to flash brightness, 67-16
- ...peripheral visual cues, 68-11, 68-12, 68-22
- ...propeller paint schemes, 78-29
- ...reaction time, flash luminance and brightness, 67-24
- ...size and distance, 62-15, 64-13, 66-22, 66-24, 67-18
- ...spatial extent, 63-20
- ...spiral aftereffect, 64-9, 64-10, 68-10, 69-15, 71-31
- ...tactile, 62-11, 62-16
- ...two-flash thresholds, 68-20, 70-15
- ...vision through sunscreen materials, 78-28

## Performance (also see: Human Factors)

- ...accident experience, physical defects, 76-7, 77-20, 79-19, 81-14, 83-18
- ...age effects, 95-3, 95-7, 99-20, 99-22
- ...age index for pilots, 77-6, 78-16, 78-27, 83-15, 85-3
- ...age 60 rule, 94-20, 94-21, 94-22, 94-23, 04-8
- ...airspace complexity, 05-16
- -and operational errors, 06-4
- ...air traffic controllers
  - -age and retirement, 05-6, 05-22
  - -age effects, 61-1, 62-3, 65-21, 67-1, 71-36, 73-7, 81-12, 84-6, 99-18, 99-23, 05-22
  - -aptitude tests for prediction, 65-19, 68-14, 71-28, 71-36, 71-40, 72-18, 79-3, 84-2, 84-6, 88-3, 89-6, 94-4, 97-15, 98-23, 99-16, 00-2, 00-12. 06-16
  - -color displays and color defect, 06-2, 06-6, 06-11, 06-15, 06-22
  - -color perception effects, 83-11, 90-3
  - -communication, ATC/pilot, 93-20, 95-15, 96-10, 96-20, 96-26, 98-17, 98-20, 99-21, 01-8, 01-9, 05-19, 06-25
  - -commuter (driving) risk factor before and after shifts, 06-13
  - -computer experience and AT-SAT performance, 00-2
  - -development of temporal markers to profile, 06-20
  - -evaluation, 61-1, 65-22, 98-23

- -experience as predictor, 63-31
- -flight service station training, 86-6
- -flashing target effects, 90-3, 97-10, 99-8
- -human factors literature review, 06-21
- -incident reporting, 65-10
- -information complexity measures in automation design, 04-17
- -information and cognitive complexity assessment methods, 05-4
- -job task taxonomy for en route, 93-1
- -measurement in air traffic selection and training (AT-SAT) simulation, 00-2, 00-12
- -memory in air traffic control, 97-22, 98-16.
- -navigation displays, 00-8, 04-20
- –Multiple Task Performance Battery for selection, 72-5, 74-10
- -napping and night shift performance, 00-10
- -no relation to age, 05-22
- operational errors, development of temporal markers to profile, 06-20
- -operational errors, human factors literature review, 06-21
- -operational errors, JANUS technique applied to causal factors, 03-21
- -operational errors/deviations, role of shiftwork and fatigue, 99-2
- -pass-fail in FSS training program, 79-18
- -personality factors, relation to, 70-14, 89-7, 03-20, 04-21
- -radar simulator, 65-31, 75-8, 77-18, 78-11, 80-15, 80-17, 82-1, 82-16, 83-9, 83-13, 86-4, 88-4, 89-1, 90-3, 95-23
- -sector characteristics, activity and complexity, 06-29
- –sector characteristics and operational errors, 87-15, 06-4
- –sex differences, 72-22
- -situation awareness, 94-27, 98-16, 99-3
- -strategies for reducing causal factors, 03-19
- -video game experience as a predictor, 97-4
- ...airworthiness inspectors, 87-4
- ...alcohol effects, 66-29, 69-14, 71-20, 71-34, 72-4, 72-11, 72-34, 78-2, 79-7, 79-26, 82-3, 83-2, 85-5, 88-2, 94-24, 95-3, 95-7, 95-24
- ...antihistamine effects, at altitude, 68-15, 78-19 –on performance, 97-25, 99-20
- ...attitude indicators (flight instrument), 73-9, 05-23
- ...attitude questionnaires to predict under stress, 69-7
- ...aural glide slope cues for instrument approaches,
- ...aviation medical examiners, 84-7
- ...chronic disulfoton poisoning effects, 69-19
- ...cockpit instrument display, compact, 75-12

- -Cockpit Display of Traffic Information (CDTI), 03-2, 03-5, 03-13, 04-11, 04-20
- -Electronic Attitude Direction Indicator (EADI), equivalence tests, 05-23
- -GPS, 98-9, 98-12, 99-9, 99-13, 00-4, 03-19
- -head-up, 98-28
- -Highway-in-the-Sky (HITS), 00-31
- -NEXRAD weather, 04-5
- ...cognitive appraisal of stress effects, 68-17
- ...cognitive style and learning, 99-12
- ...crash diet effects, 81-8
- ...decompression effects, 66-10
- ...dextroamphetamine effects during sleep loss, 75-14
- ...distractibility effects, 72-25
- ...distracting stimuli effects, 71-7, 72-14
- ...drug effects, during angular acceleration, 73-17, 82-19
  - -in aircraft simulator, 64-18
  - -on complex performance, 69-9, 75-14, 77-17, 78-19, 97-25, 99-20
- ...eye blink-rate measures, 94-17, 94-26, 96-9, 99-28
- ...flight instructors and accidents, 96-3
- ...flight simulation, 96-16, 97-9, 97-24, 98-12, 04-5, 05-23
- ...forest fire retardant missions, effects of, 68-26
- ...gender effects and antihistamine, 99-20
- ...heart disease and age effects, 64-4
- ...heat and altitude effects, 71-17
- ...heat effects on complex performance, 69-10, 72-17
- ...Human Factors Analysis and Classification System (HFACS), 00-7, 00-28, 01-3, 03-4, 05-24, 05-25, 06-7, 06-18, 06-24
- ...human factors, review of operational errors literature, 06-21
- ...hypoxia, decrement due to, 66-15, 71-11, 82-10, 83-15, 85-3, 85-5, 97-9
- ...impairment by alcohol, 66-29, 69-14, 71-20, 71-34, 72-4, 72-11, 72-34, 78-2, 79-7, 79-26, 82-3, 83-2, 85-5, 88-2, 94-24, 95-3, 95-7, 95-24
- ...instrument flying using peripheral visual cues, 68-11, 68-12, 68-22
- ...intercontinental flight effects, 65-16, 65-28, 65-29, 65-30, 68-8, 69-17
- ...laser illumination effects on flight simulator performance, 03-12, 04-9
- ...marihuana effects, 73-12, 75-6, 85-8
- ...measurement, 77-15, 78-33, 78-34, 84-2, 98-23, 99-22, 00-2, 00-5, 05-23
- ...mental task effects on auditory fatigue, 65-1, 65-2
- ...monotonous task correlates, 73-14, 75-8
- ...noise effects on simulated radar task, 79-24
- ...Phosdrin effects, 72-29, 73-3
- ...physical conditioning program effects, 66-17, 66-21

- ...physical exercise effects, 82-4, 82-10
- ...physiological measures, on perceptual-motor tasks, 69-8
  - -in severe weather flying, 66-41
- ...pilot tracking during successive approaches, 72-9
- ...pseudopilots in radar training, 80-5
- ...psychophysiological indices, 99-28
- ...readiness to perform, 93-13, 95-24, 97-5
- ...reliability of individual subjects, 78-37
- ...rotating shifts, 96-23, 99-2
  - –and commuting risk factors before and after shifts, 06-13
- ...shifts in wake-sleep cycle, effects, 75-10, 76-11
- ...signal rate effects on monitoring, 69-6, 69-16, 97-10
- ...simulated autopilot malfunctions, 97-24
- ...simulated glidepath indicators, 79-4, 79-25, 81-6, 82-6
- ...situation assessment through re-creation of incidents (SATORI), 93-12, 97-13, 98-14
- ...situation awareness, effects, 99-3, 00-31
  - -FAIT analysis for free-flight environment, 03-5
- ...sleep deprivation, effects, 70-8, 85-3
- -quality and ATC performance, 00-10
- ...smoking effects, 80-11, 83-4, 97-7
- ...sonic boom effects, 71-29, 72-19, 74-9
- ...startle effects, 69-21, 73-11, 73-16, 79-24, 83-13, 88-4
- ...stress-related decrements, 93-19
- ...student pilots, 67-15, 69-12
- ...tasks for operator-skills research, 66-19
- ...teamwork training, 99-24
- ...time-sharing ability, 76-1, 99-22
- ...tracking and complex performance, 72-21
- ...tracking, dextroamphetamine, sleep loss, 76-12
- ...video game experience, on ATC selection tests, 97-4
- ...visual search with and without radar sweepline, 79-12
- ...visual taskload effects on CFF change during complex monitoring, 85-13
- ...visual taskload effects on complex monitoring, 88-1, 90-3, 95-23
- ...weather information (NEXRAD) and simulator performance, 04-5
- ...work in heat and cold, 66-23, 68-13

## Personnel, FAA (see also, Air Traffic Controllers)

- ...airway facilities personnel, job attitudes, 77-21, 79-11, 83-7
- ...Airway Science Curriculum Demonstration Project, evaluation of, 88-5
- ...airworthiness inspectors, job performance ratings of, 87-4

- ...biological rhythms and rotating shiftwork considerations, 86-2
- ...correlates of satisfaction with training, 91-9
- ...decision making, equity, and job satisfaction, 91-10
- ...effectiveness of management training, 75-9, 78-32, 92-16
- ...electronics technicians, 97-19
- ...employee attitude survey, year 2000, process feedback, 03-11
  - -year 2003 agency-wide work attitudes, 04-22
  - -year 2003 Air Traffic Organization work attitudes, 04-23
  - -year 2003 analysis of employee comments, 05-12
- ...empowerment, predictors of perceived, 98-24
- ...ergonomic interventions to reduce work stress, 99-17
- ...flight inspection aircrews, crew resource management, 96-24
- ...flight service station, organizational climate, 97-12
- ...health awareness programs, survey evaluation, 00-3
- ...intent to leave job, and active turnover, 06-30 –job satisfaction, 91-15
- ...identification of management training needs, 90-2, 92-16
- ...identification with occupation, 92-21
- ...job task analysis for FAA supervisors, 91-5
- ...job task taxonomy, en route, 93-1
- ...maintenance, 89-9, 90-14, 91-16, 92-3, 93-5, 93-15, 94-12, 95-14, 95-31, 96-2, 05-21
- ...matrix teams, 93-18
- ...organizational change, and cynicism, 99-27, 00-14
- ...organizational commitment, 92-21
- ...organizational communication, and technology change, 99-25
- ...organizational support, perceptions of, 92-13
- ...safety perceptions following safety awareness program, 99-19
- ...team implementation and diversity climate, 00-27 ...test fairness for selection, 79-3, 96-13, 99-16

## **Pesticides**

- ...aerial application aircraft accidents, 66-27, 66-30, 68-16, 78-31, 80-3
- ...biochemical effects of lindane and dieldrin, 62-10, 63-4
- ...chlordimeform toxicity, 77-19
- ...cholinesterase determination, 67-5
- ...CNS, effects of organophosphates, 63-24, 69-19, 79-15
- ...comparison of serum cholinesterase methods, 70-13, 72-12
- ...dieldrin effects on liver, 66-5, 66-26
- ...endrin effects, 66-11, 66-26, 66-34, 70-11
- ...endrin, mechanisms of action, 63-16, 63-26

- ...methamidophos toxicity, 78-26
- ...organophosphates effects on reproduction, 70-3
- ...Phosdrin effects on performance, 72-29, 73-3
- ...Phosdrin effects on vision, 73-4
- ...storage stability of human blood cholinesterase, 70-4
- ...symptoms and treatment of poisoning, 62-8

# Physical fitness

- ...aerospace, commercial passengers, guidance for medical screening, 06-1
- ...age relationship, 63-18
- ...ATC students, 71-8
- ...field test for, 63-6
- ...myocardial infarction, 64-2, 66-17, 66-21
- ...neuropsychological screening, 92-11

# Physiology

- ...autonomic and performance, 93-19
- ...backscatter, responses to, 72-8
- ...blood donation effects, 84-4
- ...cabin water spray, following, 98-4
- ...crash diet effects, 81-2, 81-8
- ...evaporative water loss device, 67-17
- ...gas pressure in tissue, 63-11
- ...high altitude training, need for, 91-13
- ...hydrogen ion concentration, conversion table from pH, 68-23
- ...measures during complex task performance, 69-8, 82-10
- ...neural control of the ciliary muscle, 63-5
- ...protection at high altitude, 99-4
- ...sleep deprivation responses, 70-8, 75-14
- ...smoking withdrawal responses, 83-4
- ...thermal balance, 66-23
- ...tolerances to heat, 70-22, 71-4
- ...wheel-well stowaways, 96-25

### **Pilots**

- ...accident experience, physical defects, 76-7, 77-20, 79-19, 81-14, 83-18
- ...accident predisposition, 72-2, 73-5
- -organizational factors, 00-28
- ...active population, estimate of, 68-5
- ...aerial applicator protection, 66-30, 72-15, 80-3
- ...age index, 77-6, 78-16, 78-27, 82-18
- ...age 60 rule, 94-20, 94-21, 94-22, 94-23, 04-8
- ...ages of those in aircraft accidents, 67-22, 70-18, 77-10, 94-22
- ...alcohol effects on performance, 66-29, 72-4, 79-7, 79-26
- ...alcoholic airline pilots rehabilitation, 85-12
- ...altitude tolerance with pulmonary disease, 77-16

- ...analysis of certification denial actions, 68-9, 74-5, 76-10, 78-25, 80-19, 83-5,84-9, 85-9, 86-7, 90-5, 90-7
- ...anticollision observing responses, 73-6
- ...attitudes toward safety, 95-27, 05-7
  - -toward safety training, 97-16, 98-6, 99-7, 03-10
- ...attrition, 72-13, 73-8
- ...blood donation effects, 84-4
- ...blood pressure levels, 84-3
- ...cardiovascular health changes in third-class certificate holders, 72-26
- ...Cockpit Display of Traffic Information (CDTI), FIAT, 03-5, 03-13, 04-11, 04-20
- ...cockpit visual problems, 77-2, 77-7, 77-13, 77-14, 78-17, 03-12
- ...color vision and signal lights, 71-27, 71-32, 73-18, 75-1, 93-17
- ...communication, 96-10, 96-20, 96-26, 98-17, 98-20, 99-21, 06-25
- ...computer-based flight simulator, 96-15
- ...computer use, in meeting recency of experience flight requirements, 03-3
  - -in flight training, 94-25, 95-6, 96-8, 97-11
- ...control force capabilities of females, 72-27, 73-23
- ...coronary atherosclerosis in fatal accidents, 80-8, 85-6
- ...crew resource management, flight inspection aircrew, 96-24
- ...decision-making skills, 98-7
- ...decision-making training, 87-6, 96-19, 98-6
- -"expert" pilot training model, 97-6
- -use of weather information, 97-3, 97-23, 04-5, 05-7, 05-15
- ...demographics and vision restrictions, 04-6
- ...disease prevalence and incidence, 73-8, 81-9, 84-8, 89-2
- ...drug effects in aircraft simulator, 64-18
- ...engine noise and hearing thresholds, 05-12
- ...exams of first-class certificate holders by senior AMEs, 71-38
- ...experience in controller selection, 74-8
- ...fatigue, 81-13
- ...flight information accessed by pilots, 00-26
- ...flight physiology training, need for, 91-13, 03-10
- ...G effects of aerobatics, 72-28, 82-13
- ...glare exposure and accidents, 03-6, 06-28
- ...hearing, vs. non-pilots, 05-12
- ...heart rates during instrument approaches, 70-7, 71-24, 75-12
- ...heat effects on performance in a flight simulator, 72-17
- ...judgment training, 87-6
- ...laser light illumination incidents, 06-23
- ...longevity and survival of retired airline pilots, 95-5

- ...marginal weather and willingness to take off, 05-7, 05-15
- ...marijuana in general aviation fatal accidents, 85-8
- ...medical standards, 71-25, 82-14
- ...medications found postmortem and medical history, 06-12
- ...navigation displays, moving map, 04-20
  - -using text and graphics, 00-8
  - ...neuropsychological screening, 92-11
- ...noise effects on hearing, 72-32, 05-12
- ...occupations, 69-11, 77-10
- ...ozone effects, 80-9, 89-13
- ...performance, on glidepath indicator systems, 79-4, 79-25, 81-6, 82-6
- –electronic attitude-direction indicator (EADI), 05-23
- -GPS displays, 98-9, 98-12, 99-9, 99-13, 99-26, 03-17
- -head-up displays, 98-28
- -Highway-in-the Sky (HITS) display, 00-31
- -NEXRAD weather display, 04-5
- -simulated autopilot malfunctions, 97-24
- -two attitude indicators, 73-9
- ...peripheral visual cue response, 68-11, 68-12, 68-22
- ...physician accidents, 66-25, 71-9
- ...physiological responses on cross-country flights, 71-23
- ...physiological studies in air tankers, 68-26
- ...pulmonary function, 77-3
- ...risk factors for cardiac events, 90-7
- ...safety climate, pilot perception of, 00-28
- ...safety training, evaluation, 97-16, 98-6, 99-7, 03-10
- ...satisfaction with ATC services, 90-6
- ...severe weather flying, 66-41, 05-7, 05-15
- ...shoulder harness, use of, 95-2
- ...smoking effects on performance, 80-11, 83-4
- ...status variables with accidents, 70-18
- ... stress, domestic-based and perceived performance, 00-32
- ...stress in student pilots, 67-15, 69-12, 76-2
- ...suicide, 72-2, 73-5, 06-5
- ...tracking performance during successive approaches, 72-9
- ...type airman certificate related to accidents, 67-23
- ...vertigo, 67-19
- ...visual acuity, midair collisions, 75-5
- ...voice communication, 93-20, 06-25
- ...workload, 77-15, 81-13

### Pregnancy

- ...crewmember radiation exposure, 92-2, 00-33, 03-16
- ...emergency air transport, 82-5

- ...impact injuries, 68-6, 68-24
- ...organophosphate pesticide effects in rats, 70-3

# **Propellers**

- ...paint schemes conspicuity, 78-29
- ...propeller-to-person accidents, 81-15, 93-2

# Protective breathing equipment

...evaluation, 62-21, 66-7, 66-20, 67-3, 67-9, 72-10, 78-4, 79-13, 80-18, 83-10, 85-10, 87-5, 89-5, 93-6, 96-4, 98-27, 00-6, 04-3, 05-18

# **Psychology**

- ...accident proneness, 93-9
- ...air traffic controllers and retirement age, 05-6, 05-22
- ...aircraft mix and traffic complexity ratings, 05-16
- ...automation and pilot performance, 97-24, 00-8
- ...CogScreen, neuropsychological test, age effects, 99-22
- ...cognitive complexity in an air traffic control displays, 05-4
- ...cognitive style and learning, 99-12
- ...Composite Mood Adjective Check List to measure stress effects, 71-14, 71-21, 73-22
- ...cultural diversity awareness training, 95-10
- ...disability retirement, and ATC personality factors, 03-14
- ...diversity climate, 00-26
- ...empowerment, predictors of perceived, 98-24
- ...expertise method in aeronautical decision- making, 97-6
- ...FAA employee attitude survey, year 2000, process feedback, 03-11
  - -year 2003 agency-wide work attitudes, 04-22
  - -year 2003 Air Traffic Organization work attitudes, 04-23
  - -year 2003 analysis of employee comments, 05-12
- ...flight inspection aircraft, preferences, 95-18
- ...Human Factors Analysis and Classification System (HFACS) applications, 00-7, 00-28, 01-3, 03-4, 05-24, 05-25, 06-7, 06-18, 06-24
- ...human factors review of operational error literature, 06-21
- ...JANUS technique and causal factors in ATC operational errors, 03-21
- ...job attitudes, airway facilities personnel, 77-21, 79-11, 83-7
- ...memory in air traffic control, 97-22, 98-16
- ...motivation in aircraft evacuation, 96-18, 03-15, 04-2
- ...Myers-Briggs personality test with ATCSs, 04-21

- ...organizational factors, 90-2, 91-5, 92-8, 92-9, 92-10, 92-13, 92-17, 92-21, 05-1294-2, 98-23, 99-25, 99-27, 00-14, 00-27, 03-11, 04-22, 04-23, 05-12
- ...personality assessment, 71-35, 91-8, 93-4, 03-14, 04-21
- ...pilot attitudes toward safety, 95-27, 98-7, 99-7, 05-7, 05-15
- ...psychological autopsy, 72-2, 73-5
- ...psychophysiological indices of alertness, 99-28
- ...safety behaviors on the job, management influence, 97-8, 99-19
- ...Shipley Institute of Living Scale with ATCSs, 92-30
- ...situational awareness, 94-27, 97-13, 97-22, 98-16, 99-3, 00-31, 03-5, 03-13
- ...Sixteen Personality Factors test with ATCSs, 97-17, 03-14
- ...stress and anxiety in air traffic controllers, 80-14, 81-5, 89-7
- ...stress, domestic-based and perceived pilot performance, 00-32
  - -physical symptoms in employees, 99-17
- ...Type A behavior, 86-4, 94-13
- ...use of PC-based training devices, 94-25, 95-6, 96-8, 96-15, 96-16, 97-11, 03-3
- ...validity coefficients in ATCS selection, 00-15

## Pulmonary

- ...disease, altitude tolerance, 77-16
- ...function testing, 64-1, 71-8, 77-3
- ...glyceryl trinitrate, vascular effects of, 64-11
- ...hyperpyrexia, responses to, 64-8
- ...ozone effects on function, 79-20, 80-9, 89-13
- ...protection from smoke, fire, 67-4, 78-4, 83-10, 83-14, 85-10
- ...thromboembolism, 64-7

#### Radiation

- ...calibration of Concorde detection instrument, 71-26
- ...cosmic, and air carrier crewmembers, 92-2, 00-33, 03-16, 05-14
- ...measurements at SST altitudes, 71-26, 80-2
- ...RBE of fast neutrons, 78-8
- ...transport limits for radioactive material, 82-12

#### Renal function

- ...acute arterial occlusion effects, 63-22, 65-27
- ...autoregulation mechanism, 63-32
- ...insecticide effects, 63-26
- ...venous pressure effects, increase of, 62-18, 63-1

### Research, aeromedical

- ...aging studies at GCRI, 64-1
- ...aims and accomplishments, 62-20, 67-25
- ...alcohol effects review, low dose, 94-24
- ...ballistocardiography, 64-12, 65-8, 65-15
- ...beta blockers, analysis and differentiation, 04-15, 05-10
- ...bibliography of acceleration studies, 63-30
- ...bibliography of shiftwork research, 83-17
- ...butalbital, distribution of fluids and tissues, 00-29
- ...carboxyhemoglobin standard, 98-21
- ...color vision, 67-8, 71-27, 71-32, 73-18, 75-1,
- 83-11, 85-7, 92-6, 92-28, 92-29, 93-16, 93-17,
- 95-13, 96-22, 04-10, 04-14, 06-2, 06-6, 06-11, 06-15, 06-22
- ...commuting risk factors, before and after work shifts, 06-13
- ...DNA, detection of postmortem ethanol-producing microorganisms, 00-16
  - -identification of forensic samples, 06-14
- ...DNA profiling, 98-18, 99-14, 06-14
- ...enantiomeric analysis of ephedrines and norephedrines, 05-8
- ...exercise, 64-2, 66-36
- ...hearing, conservation with earplugs, 73-20, 75-11
- ...history, CAMI, prefaces to 87-1, 97-1, 98-1, 01-1, 03-1, 05-1
  - -CAMI research contributions from 1,000 technical reports, 05-3
- ...index of international publications, 93-3
- ...index of OAM reports, 63-2, 64-20, 66-1, 68-1,
- 70-1, 72-1, 74-1, 77-1, 79-1, 81-1, 83-1, 87-1,
- 90-1, 92-1, 94-1, 96-1, 97-1, 98-1, 99-1, 00-1, 01-1, 03-1, 05-1
- ...interpretation of carboxyhemoglobin and cyanide concentrations, 05-9
- ...medical care, inflight, 00-13
- ...medical incapacitation and impairment of pilots inflight, 04-16
- ...medical incidents inflight, 00-13
- ...needs, 63-35, 71-10
- ...noise effects on aircrew personnel, 72-32
- ...opiates vs. poppy seed use, postmortem determinations, 05-11
- ...postmortem, cocaine analysis, 03-23, 03-24
- -accurate assignment of ethanol origin, 04-13
- -ethanol analysis, internal standard, 98-5
- -identification of forensic specimens, 06-14
- ...plans, for NAS operator selection, 97-19
- ...radiation, galactic, 92-2, 00-33, 03-16, 05-14
- ...RNA isolation from peripheral blood cells, protocol validation, 04-1
- ...quinine elimination, 94-16

- ...stain test for dieldrin and endrin, 66-26
- ...translated material, Tech. Pub. #1, 64-16, 65-17, 66-2, 68-7, 71-5, 76-4, 81-4
- ...visual standards and tests used with aircraft maintenance personnel, 05-21

### Restraint

- ...acceptance of upper torso restraint, 71-12
- ...bibliography, 63-30
- ...center of gravity, 62-14, 65-23, 69-22
- ...child, 94-19, 95-30
- ...cockpit delethalization, 66-3, 71-3, 72-6, 81-10
- ...comparison of systems, 67-13, 69-3, 69-4, 69-5, 69-13
- ...effectiveness in agricultural aircraft accidents, 72-15, 80-3
- ...evaluation, 78-6, 78-24, 79-17
- ...head impacts while wearing, 72-6
- ...infant and child systems, 78-12
- ...kinematics with seatbelt restraint, 62-13, 92-20
- ...lapbelt effects on pregnant female, 68-24
- ...push-button buckles, 99-6
- ...shoulder harness benefits, 72-3, 82-7, 83-8
- ...shoulder harness design, 65-14
- ...sport parachutists, 98-11
- ...upper body restraint installation, 66-33

### Seat

- ...child and infant seat evaluation, 78-12, 94-19, 95-30
- ...comfort, 62-1
- ...cushion flotation, 66-13, 95-20
- ...energy-absorbing, 83-3, 90-11
- ...evaluation, 78-6, 78-24, 79-17, 80-3, 81-10, 82-7, 83-3
- ...fire-blocking materials toxicity, 86-1
- ...head injury criteria (HIC) component test device, evaluation, 04-18
- ...injury potential, 66-18, 71-3, 72-15, 82-7, 83-8, 89-3
- ...pitch and evacuation, 92-27
- ...placement and Type III exits, 95-22
- ...pressure distribution, 62-1
- ...rearward-facing, injuries, 62-7, 69-13
- ...side-facing, impact injuries, 69-13

### Seatbelts

- ...center of gravity in design, 62-14, 65-23
- ...cockpit delethalization, 66-3, 71-3
- ...evaluation of different systems, 67-13, 69-3, 69-13
- ...impact injuries due to, 69-5
- ...impact injuries to pregnant females, 68-24
- ...kinematics of restrained subjects, 62-13
- ...push-button buckles, 99-6

## Shiftwork and shift rotations

- ...attitudes of ATCSs, 73-2
- ...bibliography of shiftwork research, 83-17
- ...commuting risk factors before and after shifts, 06-13
- ...8- vs. 10-hour work schedules, 95-32
- ...5-day and 2-2-1 pattern, 73-22, 75-7, 95-12, 95-19, 96-23
- ...performance effects, shifts and antihistamines, 97-25
  - -shifts and fatigue, 99-2
- ...review, 86-2
- ...sleep in air traffic controllers, 77-5, 95-12, 95-19, 99-2, 00-10
- ...steady and 2-2-1 shifts, 85-2
- ...symptoms reported for ATCSs, 65-5, 65-6
- ...translations of reports, 81-4

### Shoulder harness

- ...acceptance tests, 71-12
- ...angle of shoulder slope in design, 65-14
- ...benefits, 72-3, 82-7, 83-8
- ...cockpit delethalization, 66-3, 72-6, 81-10
- ...comparison of types, 67-13, 69-3, 69-4, 69-5
- ...effectiveness in agricultural aircraft accidents, 72-15, 80-3
- ...failures, 81-10
- ...head impacts while wearing, 72-6
- ...installation in general aviation aircraft, 66-33
- ...use of, 95-2

### Sickle cell trait

- ...aeromedical significance, 76-15, 80-20
- ...research protocol, 78-30

#### **Simulation**

- ...advanced general aviation cockpit displays for visual flight procedures, 04-20, 05-23
- ...air traffic controller radar task, 65-31, 75-8, 77-18, 78-11, 79-12, 79-24, 80-15, 81-12, 82-1, 82-16, 83-9, 83-13, 90-3, 94-17, 94-26, 96-9, 99-3, 00-2, 00-5
- ...air traffic controller color perception and job performance, 83-11, 90-9, 92-6
- ...Air Traffic Selection and Training (AT-SAT), 00-2 –and personality test scores, 03-20
- ...aircraft passenger emergency evacuation, 72-30, 77-11, 78-23, 96-18, 97-18, 00-15, 04-2, 04-12
- ...approach control and communication, 98-17
- ...autopilot malfunctions and pilot responses, 97-24
- ...aviation stress protocol, 78-5
- ...electronic attitude direction indicator, PFD equivalency, 05-23
- ...flight, PC-based, 96-15, 96-16 -and performance, 97-9

- ...GPS displays, 98-9, 98-12
- ...head-up displays, 98-28
- ... Highway-in-the Sky (HITS) display, 00-31
- ...+Gz, 79-8
- ...laser illumination effects on pilot responses, 03-12, 04-9
- ...movement of objects in depth, 65-32
- ...navigation display formats, 96-16
- ...NEXRAD weather displays and flight performance, 04-5
- ...night approaches to landing, 77-12, 78-15, 79-4, 81-6, 82-6
- ...operator skills research, 66-19
- ...pilot workload, 77-15, 82-10, 83-15
- ...sonic booms, 71-29, 72-19, 72-24, 72-35, 73-16
- ...stress in ground trainer use, 76-2
- ...transfer of training, 69-24
- ...visual glidepath indicator systems, 79-4, 79-25, 81-6, 82-6

## Skin

- ...conductance with sonic booms, 71-29
- ...evaporative water loss, 63-25
- ...flammability of toiletries, 63-27
- ...galvanic skin response, 64-18
- ...tactile communication, 62-11, 62-16
- ...temperature to predict tolerances to heat and cold, 71-4
- ...thermal stress following cabin water spray, 98-4

### Sleep

- ...air traffic controllers, 77-5, 95-12, 95-19, 00-10,
- ...deprivation, 70-8, 85-3
- ...dextroamphetamine effects during sleep loss, 75-14
- ...loss, and performance, 93-19
- -and vestibular response, 86-9
- ...shiftwork effects in sleep-wake cycle, 75-10, 76-11
- ...sonic boom effects, 72-19, 72-24, 72-35
- ...work schedule effects, 95-32, 99-2, 00-10

### Smoke

- ...air carrier accidents, 62-9, 65-7, 70-16
- ...crew protective devices, 76-5, 78-4, 78-14, 78-41, 83-14, 89-8, 89-11
- ...emergency signs, effects on reading, 79-22, 80-13, 81-7
- ...passenger protective breathing devices, 67-4, 70-20, 83-10, 85-10, 87-2, 87-5, 89-5, 89-12, 05-18 ...toxicity, 95-8
- ...toxicity of thermal degradation products of engine oils, 83-12

## **Smoking**

...aviation safety, effects on, 80-11, 97-7 ...smoking/withdrawal effects, 83-4

## Sonic booms

...autonomic responses, 71-29, 72-35, 73-16, 74-9 ...sleep, effects during, 72-19, 72-24, 72-35

...startle effects, 73-11, 73-16, 74-9 ...tracking performance effects, 71-29

## Stalls

...warning device, 66-31

# Standards

...advanced aerospace systems, 71-33

...aeromedical, 71-25, 71-33, 82-14, 00-19

...carboxyhemoglobin, 98-21

...color vision for air traffic controllers, 83-11, 90-9, 04-10, 04-14, 06-2, 06-6, 06-11, 06-15, 06-22

...escape slides, inflatable, 98-3

...floor proximity marking systems, 98-2

...head injury criteria (HIC) component test device, evaluation, 04-18

...neurological and neurosurgical conditions, 81-3

...postmortem ethanol analysis, internal standard,

-accurate assignment of ethanol origin, 04-13

...quality assurance in forensic toxicology, 99-11, 99-15, 03-18, 04-15

### **Stress**

...air tanker pilots, 68-26

...air traffic controllers, 71-2, 71-21, 73-15, 73-21, 73-22, 74-11, 75-7, 76-13, 77-23, 78-5, 78-18, 78-40, 80-14, 82-17, 05-7

...assessment with State-Trait Anxiety Inventory, 72-23, 81-5, 91-8

...aviation stress protocol—simulation, 78-5

...Composite Mood Adjective Check List, to measure, 71-14, 71-21

...domestic-based and pilots' perceived performance, 00 - 32

...ergonomic interventions, 99-17

...evaporative water loss device, 67-17

...flight inspection crews, 81-13

...+Gz, 79-8

...heart rate and performance effects, 68-17, 69-21

...heart rates during instrument approaches, 70-7, 71-24, 75-12

...job and burnout, 92-7

...measurement of evaporative water loss, 63-25

...monotony with automation as a stressor, 80-1

...performance prediction by attitudes, 69-7

...performance under auditory distraction, 72-14

...physiological responses on cross-country flights,

...plasma catecholamine determination, 66-6, 71-15

...severe weather flying, 66-41

...situational in accident causation, 72-2, 73-5

...student pilots, 67-15, 69-12, 76-2

...symptoms reported by air traffic controllers, 65-5,

...urinary metabolites, 78-18, 78-40, 85-2

...wake-sleep cycle shifts, 75-10, 76-11

## Suicide

...aircraft accident cause, 72-2, 73-5, 06-5

# Supersonic transport

...anticollision lights, 70-9, 70-15, 71-42

...decompression profiles, 70-12, 99-4

...evacuation tests, 70-19

...radiation at SST altitudes, 71-26, 80-2

...sonic boom effects, 71-29, 72-19, 72-24, 72-35, 73-11, 73-16, 74-9

# **Temperature**

...cold effects on shipped dogs, 87-2

...changes in cold water with prototype life preserver, 85-11

...complex performance effects, 69-10, 71-17, 72-17

...evaporative water loss, 63-25, 67-17

...heat effects on shipped dogs, 77-8, 81-11, 84-5, 87-8

...heat tolerance limits of rats and mice, 86-8

...human tolerance, 62-6, 70-22

...hyperpyrexia, 64-8

...liver damage effects by dieldrin, 66-5

...maintenance of thermal balance, 66-23

...manual performance effects, 68-13

...tranquilizer effects on body temperature, 63-23, 66-14

#### **Tests**

...air traffic controller selection, 61-1, 62-2, 65-19, 65-21, 68-14, 71-28, 71-36, 72-5, 72-18, 74-10, 77-25, 78-7, 79-3, 79-14, 79-21, 80-7, 82-11,

84-2, 84-6, 90-4, 90-8, 90-13, 91-9, 94-4, 94-9,

96-13, 97-4, 97-15, 98-23, 99-16, 99-23, 00-2, 00-12, 03-20, 06-16

...alcohol abuse, 83-2

...aptitude measures, of military ATCS trainees, 71-40

–of female ATCS trainees, 72-22

...Armstrong Laboratory Aviation Personality Survey, with ATCS students, 03-20

...ataxia, alcohol effects, 79-9

...ballistocardiography, 64-12, 65-8, 65-15

...cholinesterase activity, 67-5

- ...color vision, 67-8, 71-27, 71-32, 73-18, 75-1, 83-11, 85-7, 90-9, 92-29, 93-16, 93-17, 95-13, 04-10, 04-14, 06-2
- ...complex human performance, 69-6, 69-16, 72-5, 72-21
- ...CogScreen, age effects, 99-22
- ...Composite Mood Adjective Check List, 71-14, 71-21, 73-22
- ...correlation with experience in ATCS selection, 63-31
- ...directional headings, 72-18, 90-8
- ...distraction susceptibility, 71-7
- ...emergency evacuation, 65-7, 66-42, 70-19, 70-20, 77-11, 78-3, 79-5, 89-5, 89-14, 92-27, 95-22, 95-25, 96-18, 99-10, 01-18 03-15, 04-2, 05-2
- ...energy-absorbing seat effectiveness, 83-3, 90-11
- ...equivalence tests, EADI and PFD displays, 05-23
- ...escape slides, inflatable, 98-3
- ...fairness, 79-3, 96-13, 98-23, 99-16
- ...flight service station training, 79-18, 86-6
- ...head injury criteria (HIC) component test device, evaluation, 04-18
- ...interpretation of carboxyheloglobin and cyanide concentration in aviation accidents, 05-9
- ...Myers-Briggs personality test, with ATCs, 04-21
- ...NEO Personality Inventory-Revised, with ATCS students, 03-20
- ...neuropsychological battery, 92-11, 99-22
- ...performance, 66-19, 97-5, 00-2
  - -age and disease, 64-4
  - -and age, 65-21, 71-36, 81-12, 99-23
  - -and personality factors, 70-14
  - -post decompression, 66-10
  - -with hypoxia, 66-15, 71-11, 82-10, 83-15
- ...personality assessment, 71-35, 93-4, 03-20
- ...physical fitness, 63-6, 63-18, 63-33, 64-3, 66-17
- ...proficiency in post mortem forensic toxicology, 99-11
- ...pupillary movement, 65-9, 65-25
- ...readiness to perform, 93-13, 95-24
- ...scanning and monitoring, 92-12, 94-8
- ...Shipley Institute of Living Scale, 92-30
- ...Sixteen Personality Factors test, with ATCSs, 97-17, 03-14, 03-20
- ...spiral aftereffect, 64-9, 64-10, 64-17, 68-10, 69-15, 71-31
- ...stain for dieldrin and endrin, 66-26
- ...State Trait Anxiety Inventory, 72-23, 76-13, 80-14, 81-5, 89-7, 91-8
- ...Stroop test, 71-7, 72-14
- ...supervisory, air traffic control, 92-16
- ...system for combustion toxicology, 77-9
- ...vestibular during physical exams, 75-4
- ...video game experience, 97-4

## Tobacco

...effects on aviation safety, 80-11, 83-4

### **Tolerance**

- ...brain, to concussion, 71-13, 74-4
- ...cold stress in dogs, 87-8
- ...decompression for SST, 70-12
- ...face, to impact, 65-20, 66-12, 66-40
- ...flight stresses, 62-6, 81-2
- ...free-fall impacts, 63-15
- ...heat for rats and mice, 86-8
- ...heat stress in dogs, 77-8, 81-11, 84-5, 87-8
- ...hot environments, 70-22
- ...hypoxia, propranolol effects, 79-10, 80-10
- ...impacts in water, 65-12, 68-19
- ...intercontinental flights, 65-16, 65-28, 65-29, 65-30
- ...orthostatic, 63-34, 82-3, 82-4., 92-19
- ....+Gz, 79-8, 81-2
- ...prediction for thermal environments, 71-4
- ...vertical impact, 62-19
- ...work at altitudes, 82-3

# Toxicology

- ...beta blocker, forensic analyses and differentiation, 04-15, 05-10
- ...butalbital, forensic analysis, 00-29
- ...cocaine and its metabolites, post mortem analyses, 03-23, 03-24
- ...carbon monoxide, 89-4, 93-7, 94-7, 94-18, 98-21, 00-9, 05-9
- ...combustion products of cabin materials, 77-9, 85-5, 86-1, 86-3, 86-5, 89-4, 90-15, 90-16, 91-17, 93-7, 93-8
- ...DNA, detection of ethanol-producing microorganisms in postmortem samples, 00-16
- -identification of forensic specimens, 06-14
- -profiling, quality assurance in forensic, 98-18, 99-14
- ...enantiomeric analysis of ephedrines and norephedrines, 05-8
- ...fatal aircraft accident findings, 78-31, 80-11, 82-15, 92-23, 92-24, 94-14, 97-14, 98-5, 99-29, 03-7, 03-22, 03-23, 05-9, 05-20, 06-3, 06-5, 06-12
- ...gene expression profiles, maintenance after blood storage, 04-1
- ...glucose levels, abnormal, 00-22
- ...hydrogen cyanide, 93-8, 94-7, 94-18, 05-9
- ...hydrogen sulfide, 00-34
- ...interpretation of carboxyhemoglobin and cyanide concentrations, 05-9
- ...melatonin, 98-10
- ...metabolites, 95-26, 97-14

- ...methamphetamines, 03-22
- ...methodology, single extraction urine screening, 96-17
  - -determination of poppy seed consumption vs. poppy seed use, 05-11
  - –enantiomeric analysis of ephedrines and norephedrines, 05-8
  - -interpretation of carboxyhemoglobin and cyanide concentrations, 05-9
  - -simultaneous quantification of atenolol, metoprolol, and propranolol, 05-10
- ...opiate use, postmortem determination, 5-11
- ...ozone toxicity, 80-16, 89-13
- ...postmortem ethanol analysis, internal standard, 98-5
  - -accurate assignment of ethanol origin postmortem, 04-4
  - -preservation of tissue samples, 04-4
- ...postmortem medication findings and pilot medical history, 06-12
- ...proficiency testing, 99-11
- ...quality assurance and quality control, 99-11, 99-14, 99-15, 99-29, 03-18, 04-1, 04-4, 04-13, 04-15, 06-14
- ...RNA isolation from peripheral blood cells, protocol validation, 04-1
- ...selective serotonin reuptake inhibitors (SSRIs), 03-7
- ...sildenafil (Viagra), method for detecting in postmortem samples, 00-20, 06-3
- ...thermal degradation of engine oils, 83-12
- ...time to incapacitation, 89-4, 93-7, 93-8, 94-7
- ...Vardenafil (Levitra), method for detecting in postmortem samples, 06-17

# **Training**

- ...air traffic controllers, 78-10, 79-3, 79-18, 80-5, 80-15, 82-2, 83-9, 84-6, 88-3, 89-6, 89-7, 91-9, 91-18, 94-8, 95-16, 97-15, 98-8, 98-22, 98-23, 99-16, 00-12, 04-21
- ...aviation medical examiners, 84-7
- ...biographical factors in ATCS success,83-6, 84-6
- ...correlates of satisfaction with, 91-9
- ...crew resource management, flight inspector aircrew, 96-24
- ...devices, 96-6
- ...disorientation familiarization, 70-17, 77-24
- ...diversity awareness, 95-10
- ...flight, PC-based training, 94-25, 95-6, 96-8, 97-11, 03-3
- ...flight instructors, 96-3
- ...flight physiology, need for, 91-13, 03-10
- ...flight service station, 86-6, 91-4
- ...judgment training for pilots, 87-6, 98-6

- ...maintenance personnel, 91-16, 93-5, 95-14, 95-31, 96-2
- ...management training, effectiveness of, 75-9, 78-32
- ...needs for managers, 90-2
- ...personality factor in ATC, 93-4
- ...physiological, 10-year chamber experience, 77-4
- ...reception of distorted speech, 73-13
- ...resource management, controller/crew, 95-21
- ...safety seminars for pilots, evaluation, 97-16, 99-7
- ...situation awareness, 94-27
- ...stress in pilot training, 67-15, 69-12, 76-2
- ...supervisory, air traffic control, 92-16
- ...teamwork, 99-24, 00-24
- ...test fairness, 79-3, 96-8, 99-16
- ...tracking performance during successive approaches, 72-9
- ...transfer from simulation, 69-24, 94-25, 95-6
- ...water survival programs, analysis, 98-19

# **Translations**

- ...aviation medicine, general, 64-16, 65-17, 66-2, 68-7, 71-5, 72-16, 73-19, 76-4, 81-4
- ...color vision tests, 67-8
- ...nystagmus and vestibular function, Tech. Pub. #1, 1963

#### Turbulence

- ...effects of severe weather flying, 66-41
- ...injuries, cabin safety data bank, 79-23, 82-8

### Vertigo

- ...Coriolis stimulation, 67-19
- ...flicker, 66-39
- ...illumination during angular deceleration, 68-28
- ...in-flight case with unconsciousness, 63-21
- ...production by spiral aftereffect, 64-9, 64-10, 64-17

#### Vestibular function

- ...adaptation, 66-37, 67-6, 67-7, 67-12, 67-19, 69-20, 74-3
- ...alcohol effects, 71-6, 71-16, 71-20, 71-34, 71-39, 72-34, 79-9
- ...arousal effects, 62-17, 63-29
- ...caloric habituation, 63-14, 64-14, 65-18, 67-2
- ...dextroamphetamine and secobarbital effects, 73-17
- ...habituation to rotation, 63-13, 65-24, 68-2
- ...motion sickness susceptibility, 76-14
- ...rotation device, 64-15
- ...secondary, tertiary, and inverted primary nystagmus, 63-3
- ...sleep loss effects, 86-9
- ...tests during physical examinations, 75-4
- ...translation of reports, Tech. Pub. #1, 64-16, 65-17, 66-2, 72-16, 73-19

### Vibration

...bibliography, 63-30

# Video games

...experience and air traffic scenario test score, 97-4

# Vigilance

- ...eye blink rate and fatigue, 94-17, 94-26, 96-9, 99-28
- ...hypoxia effects, 71-11
- ...napping and ATC performance, 00-10
- ...psychophysiological indices, 99-28
- ...simulated ATC tasks, 77-18, 78-11, 80-17, 94-6, 94-26, 95-23

## Vision

- ...acuity, pilots in midair collisions, 75-5
- ...age and binocular fusion time, 66-35
- ...aircraft maintenance inspectors, visual standards and tests, 05-21
- ...alcohol effects, 78-2, 79-15
- ...anticollision lights, 66-39, 70-9, 70-15, 71-42, 72-8
- ...aphakia, accident risk assessment, 95-11 -incidence in airmen, 91-14, 92-14, 93-11
- ...artificial lens implants, 92-14, 93-11
- ...atropine and Phosdrin effects, 73-4
- ...bifocal effects on radar monitoring, 82-16
- ...bright lights and visual disturbances during nighttime flight operations, 06-28
- ...Broca-Sulzer phenomenon, 68-27
- ...chart readability, 77-13, 78-17
- ...color, diagnostic tests, 67-8, 71-27, 71-32, 73-18, 75-1, 93-16, 93-17, 95-13, 96-22, 04-10, 04-14
- ...color perception and ATCS job performance, 83-11, 85-7, 90-3, 92-6, 92-28, 92-29, 04-10, 04-14, 06-2, 06-6, 06-11, 06-15, 06-22
- ...contact lenses in an airline accident, 00-18 –in certification, 90-10, 00-18
- ...cues for approach and landing, 79-4, 79-25, 81-6, 82-6
- ...deficiencies in accident airmen, 81-14, 83-18, 93-11
- ...disorientation, 69-23, 70-2
- ...drug and pesticide effects on visual reflexes, 79-15
- ...fatigue effects on binocular fusion time, 69-1
- ...fixation effects on nystagmus, 67-12
- ...gender differences in refractive surgery, 00-23
- ...glare, 94-15, 03-6
- ...glaucoma, visual field and altitude, 91-1
- ...illusions, 70-2, 71-22, 77-12, 78-15
- ...instrument readability by senior pilots, 77-2, 77-7
- ...laser illumination effects, 03-12, 04-9, 06-23
- ...light adaptation device, 66-38

- ...matching flash loudness and brightness, 67-16
- ...monitoring performance on simulated radar task, 80-17, 81-12, 82-16, 90-3, 94-17, 94-26, 96-9
- ...occupational vision, 96-12, 96-27
- ...ophthalmic lenses for air traffic controllers, 96-12, 96-27
- ...perception of depth, 63-10, 63-28, 67-20
- ...perception of size and distance, 62-15, 64-13, 65-11, 66-22, 66-24,67-18
- ...perception of spatial extent, 63-20
- ...peripheral visual cues, 68-11, 68-12, 68-22
- ...photorefractive keratectomy, 98-25
- ...presbyopic individuals, 77-14
- ...propeller paint schemes conspicuity, 78-29
- ...reaction time, flash luminance and brightness, 67-24
- ...radial keratectomy, 98-25, 06-9
- ...radial keratotomy, 99-6, 00-19, 06-9
- ...readability of emergency signs in smoke, 79-22, 80-13, 81-7
- ...refractive surgery, 99-6, 00-19, 00-23, 06-9
- ...restrictions and pilot demographics, 04-6
- ...search performance with radar sweepline, 79-12
- ...smoke-protective goggles, 76-5, 78-41, 83-14
- ...spiral aftereffect, 64-9, 64-10, 64-17, 68-10, 69-15, 71-31
- ...stimulation during angular deceleration, 68-28
- ...sunscreen materials effects, 78-28
- ...test for monitoring and scanning, 92-12, 94-8
- ...two-flash thresholds, 68-20, 70-15, 71-42
- ...X-Chrom lens to improve color vision, 78-22

### Warning signals

- ...blink amplitudes and attention, 97-10, 99-8
- ...color and flashing radar targets, 90-3
- ...pilot hearing thresholds, 05-12

#### Water survival

- ...ditching, factors in passenger flow rates, 04-12
- ...flotation, use of seat cushion, 95-20
- ...life preserver evaluations, 85-11, 03-9
- ...training programs, analysis, 98-19

# Weight

- ...accident rate relation to body weight, 70-18
- ...ATCS population, changes in, 71-19, 72-20
- ...errors in stated estimates, 73-10
- ...third-class certificate holders, changes in, 72-26

## Work

- ...age and retirement of air traffic controllers, 05-6, 05-22
- ...age effects on tolerance, 63-33
- ...alcohol effects, 82-3
- ...altitude effects on tolerance, 63-33, 82-3

- ...anxiety, relation to workload in ATCSs, 73-15, 77-23, 80-14, 81-5
- ...blood pressure effects, 66-36
- ...capacity, after myocardial infarction, 64-2, 66-17, 66-21
  - -of ATCS students, 71-8
  - -related to age, 63-18
  - -with step test, 64-3
- ...communication, and controller workload, 01-8
- ...distractibility with monotony, 72-25
- ...domestic-based stress, effects on work environment, 00-32
- ...drug effects on performance, 63-12, 63-34
- ...energy cost on treadmill, 62-5
- ...fitness, field test for, 63-6
- ...human tolerance, 62-6
- ...measurement, of air traffic controller workload, 98-15, 05-16, 06-29
  - –of information complexity in automation design, 04-17
  - -of pilot workload, 77-15, 81-13

- ...monotonous task performance correlates, 73-14 ...motivation of ATCS, 73-2
- ...organizational climate, ATC, 04-23,
  - -FAA, 98-24, 03-11, 04-22, 04-23, 05-13, 06-30 -FSS, 97-12
- ...passenger workload and protective breathing requirements, 87-2
- ...safety climate, 97-8, 99-19
- ...shift rotation effects, 65-5, 65-6, 81-4, 82-17, 83-17, 85-2, 86-2, 06-13
- ...shiftwork and performance, 97-25, 99-2, 00-10
- ...sickle cell trait effects, 80-20
- ...strength and endurance of female pilots, 72-27, 73-23
- ...strength of flight attendants, 75-13
- ...thermal balance in heat and cold, 66-23, 68-13
- ...workload effects, on complex performance, 83-15 –flight progress strips, 98-26