sublimation nuclei, depending on the environment in which they are formed.

FORMATION OF CONDENSATION NUCLEI

Many types of submicroscopic particles serve as condensation nuclei. Some of their properties may be studied by introduction into the continuous cloud chamber.

An effective method of doing this is to isolate the particles in an external storage chamber and then introduce a sample of the suspensoid by a pressure or suction system. This should be constructed to permit the controlled introduction of about 1 cc. of air containing the condensation nuclei. If introduced from a glass tube projecting several inches below the top plate, the air parcel appears as a tiny inverted mushroom-shaped cloud which falls toward the bottom of the chamber at a rate dependent on the number and size of the particles and the amount of moisture available to cause them to grow. The "stem" of the mushroom becomes greatly elongated with time and finally appears as a fine thread containing only a few particles in its cross-sectional area. This type of experimental approach permits the observation of single particles and thus becomes a useful tool in the quantitative study of nuclei.

MICROSCOPIC STUDIES OF CLOUD PARTICLES

The reactions that occur within the cloud chamber may be observed visually but with more detail through a low-power binocular microscope or by subsequent microscopic studies of samples of precipitation obtained at the floor of the chamber.

For sampling snow crystals the replica method (*6*) is the most convenient. For sampling liquid droplets the use of a sooted slide (*7*) is the easiest of several techniques available. The sampling slide is introduced by means of a rod and cylinder which slips into the tube shown in Figure 1. The slide is held within the cylinder until it has reached ambient temperature. It is then exposed, withdrawn, and permitted to warm up to room temperature in dry air.

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Analytical Methods Used in Air Pollution Study

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A voluminous literature on air pollution is now being laid down from efforts to meet the growing problem of industrial and domestic effluents. Analytical methods of the postwar period are summarized here and those trends which may be expected to influence the determination procedures of the future are delineated. The notable contribution during the period has been the Los Angeles smog investigation, in which methods of wide diversity and great ingenuity have been employed by both the county group and Stanford Research Institute. In the aerosol field new engineering developments and advances in toxicology have focused attention on submicron particles. Thus there is increasing application of the electron microscope and accelerated work on collection techniques which avoid agglomeration or dispersion effects. Gas and vapor analysis is marked by clever exploitation of spectrometry: Infrared and mass spectrometer methods are gaining ground. There is emphasis on low temperature collection procedures. New understanding of the important effects of meteorological variables combines with increased laboratory costs to establish the importance of direct-reading continuous techniques, both for control and environmental exploration work. New developments in such apparatus are being vigorously pursued. There is stronger emphasis on laboratory study of air pollution systems, a trend which may influence analytical field methods of the future.

THE analytical approach in air pollution studies today generally reflects the higher level of technical interest in the field during the postwar period. Following the war, atomic energy developments demanded serious study of radioactive effluents and this was carried out by the Advisory Stack Gas Working Group in the United States. Advances in knowledge of stack discharge were made by this group, and publication of a large volume of original wartime research on meteorology and behavior of aerosols was arranged, forming the A.E.C. "Handbook on Aerosols" (*93*). The most recent influence on the analytical approach to the air pollution problem has resulted from the Donora (*94*) and Los Angeles episodes. These investigations in which effects of pollution on health played a major role have revealed the complexity of urban air pollution phenomena and have led to analytical methods of wide diversity and great ingenuity—methods specifically adapted for exploration of the environmental etiology of pollution disease.

During 1949 and 1950, six important technical conferences on air pollution, with published proceedings, have been held in the United States (*1, 2, 38, 39, 68, 84*). These conferences have had the effect of bringing together the diversified literature on analytical methods which involves contributions from so many branches of chemistry and physics. Recently a committee on analytical techniques in air pollution has been set up under the American Society for Testing Materials. A monthly column by McCabe in Industrial and Engineering Chemistry now covers new developments in the air pollution field.

The purpose of the present paper is to summarize the analytical work of the postwar period and to delineate those trends which may be expected to influence the determination procedures of the future. Currently the aerosol literature predominates over the gas and vapor aspects, reflecting possibly the greater technical problems in aerosol measurement if not a stronger general interest in particulate pollution.

WORK ON AEROSOLS

Analysis of aerosols has been directed toward estimating such quantities as number of particles per unit volume, distribution of sizes, mass concentration, and identification through knowledge of chemical composition and physical state; choice of characteristics for measurement has been in greater measure due to interest in economic and nuisance effects of pollution; and the choice has tended to be intuitive where health effects of pollution have been involved owing to the scant toxicological knowledge on which to proceed.

AEROSOL COLLECTION TECHNIQUES

Collection techniques, as a preliminary to analysis, have been discussed by a number of authors during the past few years, notably Setterlind (*73*), Stokinger and Laskin (*89*), Magill (*57*), Smith (*81*), LaMer (*48*), Brunetti (*10*), Munger (*63*), Cholak (*18*), and in the A.E.C. "Handbook on Aerosols" (*93*), as well as in the annual reports of the Los Angeles (*51, 83*) and other air pollution agencies.

Gravity Settling, Filtration, and Scrubbing. Possibly the oldest method for obtaining samples of air-borne pollution—gravity settling—continues to find wide use in dust-fall surveys and where submicron particles of long settling time may be ignored. Filtration collection has been summarized by Silverman (*76*). It has been used in certain high volume sampling techniques (*6, 77*) and in the Donora investigation (*94*). In the Los Angeles smog research, filtration has been employed for determination of elemental sulfur, sulfuric acid mist, oil droplets, and atmospheric fluorides (*56, 57*). Molecular filter membranes have been developed by Goetz (*27*). Clogging, breakdown, and difficulties of separation from filter media have limited the application of filtration. Additionally, it must be observed that many media in common use have not been subjected to positive test for submicron retention. The Venturi scrubber has been adapted by the Stanford Research Institute in an apparatus capable of scrubbing large quantities of air with recirculated water (*59*).

Impingement. Impingers in series remain standard equipment in stack sampling for dust loading (*52*). Some modifications for such use, involving sampling tubes and application to collection of oil mists and fumes, have been described by Kunkel and McMahon (*46*). For quantitative work in particle size distribution, the impinger is more rarely employed owing to the danger of shattering particles (*3*) and to the reduced collection efficiency in the submicron range. The cascade impactor, originally developed by May (*61*), was modified by Sonkin (*82*) in 1946. Magill (*57*) reported low collection efficiency for particle sizes down to 0.2 μ in comparison with thermal precipitator. Addition of a filter paper stage was made by Laskin (*50, 89*) to collect small particles not captured by the four-jet system. Uniform collection between 0.3 and 50 μ is claimed and shattering is stated to be largely overcome. In Great Britain, Hamilton *et al.* (*36*) have measured the effect of adhesive film thickness on the sampling efficiency of the Konimeter.

Thermal Precipitation. The recent literature establishes the thermal precipitator as the collection instrument of choice for solid particle size work in the submicron range. The early designs by Green and Watson (*29*) were adapted for sampling of mine dust directly upon electron microscope screens by Watson (*101*) in 1943. Walton, Faust, and Harris (*98*) in England in 1946 and later Wilson, Laskin, and Meier (*102*) in the United States described oscillating precipitators which ensure uniform deposition and reduced microscopy to obtain representative counts. Walton (*97*) reports 100% sampling efficiency down to 100 A. diameters. Laskin (*50*) reports an upper size limit of 20 μ. Recently Bredl and Grieve (*9*) in Great Britain have described a thermal precipitator permitting gravimetric estimation of solid particles in flue gas.

The Conifuge. A new British centrifuge instrument, the conifuge, by Sawyer and Walton (*71*) appears to offer the advantage of spectrum sizing. Particles are deposited, according to their settling velocities, in a continuously graded sample on a glass slide. For particles of similar shape and density, settling velocities are a function of size. Where shape and density vary, spectrum sizing is departed from to varying degrees. Range is claimed to be 0.5 to 30 μ for sphericals of unit density.

Electrostatic Precipitation. Collection of samples of aerosols for chemical analysis and other determination procedures in which diffident handling is not a requirement is now carried out generally by electrostatic precipitation. In the Donora investigation, Clayton (*19*) used a modified Mine Safety Appliance Co. precipitator. Magill (*57*) describes the use of the household-type Westinghouse precipitron which permits 1200 cubic feet of air to be handled per minute. Magill (*57*) and Brunetti (*10*) have used a precipitator with rotating stainless steel plate partially immersed in conductivity water or dilute sulfuric acid for collection of sulfuric acid mist and other compounds; collection of droplets between 1000 and 0.3 μ is claimed. Barnes (*5*) draws attention to the limitation that collection must not exceed a maximum beyond which blowoff of clumps occurs. Precipitation directly on a microscope slide is possible and Bourne and Fosdick (*7*) have electrostatically precipitated mist and dust on hemocytometers. It is of interest that Riedel (*69*) in 1943 collected particulate matter on electron microscope screens by placing these on a long cylindrical electrode of an electrostatic precipitator.

ANALYSIS OF COLLECTED AEROSOLS

Collected aerosols suit mass concentration and bulk chemical determinations. However, particle identification and size determination appear to stand in an unsatisfactory position currently. A significant proportion of particles and droplets are submicron size. Conventional determinative methods on such material are difficult and at best yield incomplete descriptions of characteristics. Workers in this field fear the agglomerating and dispersing effects of gross manipulation of samples inherent in most methods of identification and sizing. The light microscope has proved to be limited at a size range where new interest is growing.

The Electron Microscope. The notable development in analysis of collected particulate matter must surely be the increasing application of the electron microscope. This instrument was successfully applied in studies of submicron asbestos dust as early as 1941 by Kuhn (*45*) and Ruska (*70*) in Germany. In 1943, Watson (*101*) studied quartz dust, in blasting and drilling operations, with the Toronto microscope. During the war, the electron microscope served in filtration studies as a direct method of assessing efficiency. Investigation of the etiology of Shaver's disease in 1948 by Jephcott *et al.* (*42*) showed that the incriminated fume was largely of submicron size. Gitzen (*26*), studying similar fume, identified free silica by a combination of chemical and electron microscopic techniques. Dautrebande and coworkers (*23*) differentiated quartz and sodium chloride crystals under the microscope. Meanwhile, an extensive literature on use of the microscope for particle size determination grew. An important paper by Watson (*100*) in 1948 established that a practical rationale for counting and size distribution analysis was indeed possible, in spite of the problem posed by the enormous magnifying power involved. Sharpe (*74*) described in 1949 an electron microscope graticule for more rapid particle size analysis.

The electron microscope has been applied in the air pollution field by the scientific group under the Los Angeles Air Pollution Control District (*54*) for the characterization of submicroscopic stack effluents and the classification of pollution sources. Direct collection on microscope films was obtained by adapting the thermal precipitator. Cadle and coworkers (*14*) at Stanford Research Institute used an R.C.A. console unit for examining naturally and artificially produced smog aerosols. Chromium shadowing was employed. McMurdie (*55*) discussed general aspects of electron microscopy in the aerosol field and stressed that shape of particles could be visualized by metal shadowing; identification between kaolinite and leucite particles was described, both being close diffracters by x-ray and smaller than optical microscopy would reveal.

The oustanding position of the German workers prior to 1940 is being regained. Four microscopes including a new AEG unit have been in operation for the past year on studies of industrial dust. In the author's laboratory, a new Philips unit is now being used in two studies—one involving efficiency tests for a method of collecting arsenic trioxide from roaster fumes; the other involves examination of particulate matter from the Windsor-Detroit survey of the International Joint Commission. This Philips instrument permits electron diffraction on individual particles. Additionally, x-ray diffraction and microchemical techniques are being employed for identification. The purpose of the study is to characterize as completely as possible solid pollution in the area, down to the 25 A. resolving power of the advanced Philips unit. This approach is based upon a point of view, which developed following the Donora disaster, that certain fine particulates may not necessarily be toxic per se, but may act as condensation nuclei, absorbers, or catalysts for a wide range of toxic materials originally discharged in the gaseous state and effective through chemical change, addition, or synergism to produce a respiratory load of toxic power. The progress of the work will be reported in the literature at a later date.

It may be anticipated that the electron microscope will permit an increasing measure of identification as well as rapid size distribution measurements and will make for important contributions to knowledge of the wide range of aerosols beyond conventional visualization and microanalysis.

Microchemical and Other Techniques. Microchemical identification of collected aerosols was reported at the First National Air Pollution Symposium in 1949 by Crozier and Seely (*21*). The micrurgic technique as used in the Los Angeles study was subsequently described by Cadle (*11*) who found that particles down to and including 5 microns were generally tractable, though in some cases even particles as large as 100 microns presented analytical difficulties. Saylor (*72*) dealt with microscopical recognition of particulate pollutants in an interesting paper at the Washington conference in 1950. Friedel (*25*) has described the use of mass, infrared, and ultraviolet spectrometry in analysis of collected aerosols in Los Angeles.

Certain new analytical methods, developed for analysis of collected samples in other fields, hold significance for air pollution investigation. Peterson and coworkers (*66*) describe spectrophotographic microdetermination of beryllium in air dust samples, containing from 0.05 to 200 micrograms of beryllium per sample and a variety of contaminants which interfered with methods previously available. Urone, Druschel, and Anders (*92*) have developed polarographic determination of chromium in dusts and mists, demonstrating the broad applicability of the instrument. Application of mass spectrometry to solids as exemplified in the recent paper by Gorman, Jones, and Hipple (*28*) suggests that this new technique will find important application in analysis of collected particulate matter.

A proton-scattering apparatus developed at California Institute of Technology has been employed on molecular layers of particulates collected from the Los Angeles environments (*58*). Pigford (*67*) has photographed spray droplets after collection on a greased slide. The technique involves scanning a transparent photograph with a parallel light beam of rectangular cross section. Electronic counting of beam interruptions leads to statistical analysis and computations of size distribution. Finally, there has been some toxicological interest in surface area measurement (*88*), and Innis (*40*) has recently described apparatus and procedure for rapid automatic absorption, surface area, and pore volume measurements.

DIRECT ANALYSIS OF AEROSOLS

The direct approach to aerosol study is largely exemplified in the air pollution field by efforts to determine mass concentration, particle size, and distribution. Some success has attended direct methods for chemical analysis of droplets by contact reaction with impregnated media.

Photographic Photometry and Other Visibility Instrumentation. An interesting development in direct measurement of air pollution has been the photographic photometer of Steffens (*86*), which attempts to measure the reduction in visibility by smog through photography of distant objects. The accuracy of the method is subject to a number of variations, including nonuniformity along the path of view, and to certain characteristics of the objects viewed. In a subsequent paper, Steffens and Rubin (*87*) employed standard black objects at different distances to measure attenuation coefficients over short observational paths; filters permitted comparison of attenuation coefficients for different wave lengths. These experiments yielded some data on particle size but uncontrollable variables beset the method. The principle of the photographic photometer was subsequently adapted to continuous recording of visibility by Chaney (*16*).

Tyndallometry by LaMer and Coworkers. The important fundamental studies of LaMer and coworkers (*49, 80, 93*) at Columbia University on monodispersed systems of spherical aerosols have clearly demonstrated the difficulties which lie in the way of direct absolute measurement of concentration and size distribution on complex air pollution systems. Scattering, polarization of scattered light, and transmission prove to be strong functions of particle size, shape, and refractive index. Where pollution is of relatively constant character, as for instance in relation to particular industrial operations in unpopulated areas, LaMer's instrumentation and techniques should prove of usefulness. The exceptional sensitivity of the forward angle Tyndallometer (*49*) is to be noted. Recent work by LaMer (*47*) on the growing of small homogeneous aerosol droplets holds some interest in relation to condensation nucleus research. The potentialities for particle measurement in light scattering and gravity settling techniques have been dealt with by Sinclair (*78, 79*).

Other Direct Measurement Instruments. Extensive use of the Owens automatic recording air filter for mass concentration measurement in Great Britain was reported by Parker and Richards (*64*) at the United States Technical Conference on Air Pollution. Further information on the smoke filter (*24*) was given. A transmission device for estimating density of laboratory-produced sulfuric acid mists has been employed in the 1950 smog investigations of Stanford Research Institute (*8, 83*). The continuous recording condensation nuclei meter of Vonnegut (*96*) is of interest in light of current attention to the role of fine particles in condensation of gaseous pollutants. The original photoelectric particle counter developed by Gucker and coworkers (*33*) has recently been multiplied in sensitivity (*30, 31*), though the instrument is applicable only to dilute aerosols of near uniform character. Gucker (*30*) also reports on a photoelectronic counter in which pulses of scattered light from aerosols flowing through a cell under dark-field illumination are collected upon a photosensitive tube. The instrument is said to count spherical aerosols down to 0.5 μ at rate of 1000 per minute. Gucker and O'Konski (*32*) have also adapted the electrostatic particle counter of Guyton (*34*) to particles below 3 μ in diameter.

A further report on the development was rendered in 1950 (*30*). This group has also worked with a sonic technique. Cassel (*15*) has attempted a sonic method of size determination in which oscillation of atomized aluminum dust is dark-field illuminated and photographed through a microscope. Chaney (*16*) photographed under dark field, light from particles moving into range of focus of a 35-mm. camera.

Laboratory Production of Aerosol Pollutants. Laboratory production of aerosols is of interest to experimenters. The toxicological literature is replete with methods for producing controlled concentrations of simple contaminant systems in air. The smog chamber at Stanford Research Institute (*12*, *83*) is possibly the first reported example of such equipment in the more complicated pollution field. Particulate matter was dispersed by the method of Dautrebande (*22*). Oil was particulized by the May generator (*60*). LaMer and Sinclair (*93*) developed a homogeneous aerosol generator. These workers also employed a pneumatic dispersion device and a gas ejection bomb. It would seem that an increasing amount of work under controlled laboratory conditions will be necessary in delineating the complexity of chemical and physical variables operating in the urban environments.

ANALYSIS FOR GAS AND VAPOR POLLUTANTS

Analytical methods used for determination of gases and vapors in air pollution study have, as in the case of aerosol techniques, been influenced by the economic, meteorological, and physiological considerations involved in the particular studies undertaken. Thus, sulfur dioxide measurement predominated at Trail and in many past studies owing to its corrosive action. More recently at Donora, respiratory crises and cardiovascular failures of tragic proportions focused attention on a wide range of gaseous effluents, for these effects could not be explained by sulfur dioxide concentrations alone. Most novel developments in gas and vapor analysis have resulted from the search for lachrymators and haze producers in the Los Angeles smog investigation. There is to date a voluminous literature on gas and vapor pollutants in the field, although findings on laboratory-controlled pollution systems are scant. Indications are that gases and vapors will be found to exert their full deleterious effect on health in association with particulate pollutants and normal atmospheric elements including radiation as originally predicted by Johnstone (*43*) in 1948. Such a development will create demand for gas and vapor methods capable of accurately measuring and differentiating subphysiological levels.

Gas and Vapor Collection. Collection of gases and vapors from air in recent studies has, on the whole, followed conventional lines. The Leicester survey (*24*) in Great Britain was based upon the two established techniques—volumetric sulfur dioxide apparatus and the lead peroxide method. Trials of an hourly sulfur dioxide apparatus and a directional lead peroxide device are reported. The latter was not recommended. At Donora fritted glass bubblers, evacuated flasks, and standard impingers were employed (*94*). Stanford Research Institute workers have used the portable Venturi scrubber (*59*) for aldehydes, ammonia, sulfur dioxide, and nitrogen oxides; freeze-out techniques (*13*) for organic chemicals, polyethylene bags having capacities of 10 cubic feet, absorber trains and bottles, activated carbon, and silica gel. For collection of oxidants a spray contactor with buffered potassium iodide was employed (*85*) according to the method of Crabtree and Kemp (*20*). The Los Angeles County group has used the freeze-out technique in collecting organic chemicals and the electrostatic precipitator for collection of liquid aerosols resulting from organic combustion. A high-volume activated-carbon collecting unit has been commercially developed (*53*).

Analysis of Collected Samples. Conventional chemistry has characterized the larger part of recent analytical work on collected samples of the common gaseous pollutants, although new spectrometric instruments are gaining ground. Low sulfur samples at Donora were handled by Volmer and Frolich's modified turbimetric method (*95*) and fluorides by the Talvitie colorimetric technique (*90*) using thorium-alizarin reagent. The Stanford Research Institute group has estimated oxidant potential by electrometric titration of iodine liberated from the collecting solution and by bleaching of sodium indigo sulfonate (*85*); organic chlorides have been determined by mass spectrometer. This group has also exploited the infrared spectrometer and detected oxygenated hydrocarbons, thiophenes, and the carbon-chloride bond; paraffins and C_nH_{2n} materials, either cyclic or olefin, as well as oxygenated organic compounds have been identified in samples from air by mass spectrometry; chromatographic techniques have confirmed the presence of aldehydes and organic acids. Washburn and Austin (*99*) have described the mass spectrum of a Los Angeles air sample. At the Washington conference (*68*) White, Yoe, and Friedel dealt with the scope of application of fluorimetry, colorimetry, and spectrometry, respectively.

Atkin (*4*) has developed the analysis of sulfur dioxide in the presence of sulfur trioxide, a problem which will possibly concern more chemists as fundamental studies on laboratory pollution systems grow. Jacobs (*41*) has covered methods for the differentiation of sulfur-bearing components of air contaminants. Happ, Stewart, and Brockmyre (*37*) have trapped, and analyzed with good accuracy by mass spectrometry, five-component mixtures of methylene chloride, acetone, ethylene dichloride, propylene dichloride, and cyclohexanone in nitrogen, from air at levels under 100 p.p.m. for each component. Shepherd and coworkers (*75*), employing filtration and thermal distillation or sublimation at low temperatures, have determined decimal parts per million of pollutants by mass spectrometry.

Direct Reading Methods for Gases. Direct reading methods for determining gases in air have become more associated with control than exploration in the air pollution field. Nevertheless as Haagen-Smit (*35*) has observed, intangibles may be introduced by removing atmospheric elements from the air into collection environments. Furthermore, the best examples of direct gas and vapor measurement are attainable on a continuous recording basis. It is also a reality that meteorological conditions act throughout the 24 hours. To describe the ebb and flow of pollution accurately, around-the-clock measurement is required. For survey or control work on this schedule, economy of analysis by nonautomatic procedures can rarely be justified. The Donora investigation has clearly indicated the importance to public safety of continuously recording certain pollutants, such as sulfur dioxide, in inversion areas.

In the air pollution field sulfur dioxide is the outstanding example of the application of direct and continuous measurement, although some other common effluents have been monitored in local situations by such means. Several papers on automatic recording were presented at the Washington conference and development of automatic apparatus for sulfur dioxide determination continues actively. Perley and Langsdorf (*65*) described improvements and limitations in the L and N recording Thomas autometer. Katz (*44*) has applied photoelectric automaticity to determination of low concentrations of sulfur dioxide by dilute starch-iodine, the instrument being adapted for smelter areas where hydrogen sulfide is not likely to occur. Thomas and Ivie (*91*) have described new automatic apparatus. These workers gave account of a conductivity device in which sulfur dioxide is converted to sulfuric acid by hydrogen peroxide. A second machine of continuous counterflow type records concentration instantaneously and also averages over a definite period of time. Special modifications of this apparatus were made to determine hydrogen sulfide, organic sulfur compounds, and organic chlorine and phosphorus compounds, as well as sulfuric acid aerosols. The construction of a hydrogen fluoride analyzer was reported. These instruments would appear to hold an important position in relation to new exploration work as well as to effluent control. At the Washington conference, Washburn and Austin gave a further report on the Titrilog (*68, 99*). These investigators claim for their instrument ability to determine both hydrogen sulfide and sulfur dioxide individually and simultaneously.

The development of direct reading apparatus is active throughout the whole field of gas analysis. Spectrometric methods, particularly, are being cleverly exploited. A mobile infrared spectrometer for rapid on-the-spot analysis has been designed by Chapman and Torley (*17*). Miller and coworkers (*62*) engaged in alveolar ventilation studies, have developed a portable mass spectrometer capable of continuous analysis of five different gases every 20 seconds with an accuracy of approximately 1%. The third annual review on fundamental analysis in *Analytical Chemistry*, 1951, presents an encouraging prospect for the solution of the gas analysis problems of future air pollution investigations.

CONCLUSION

In concluding this review of analytical methods used in air pollution study, particular reference can be made to the variety of techniques employed in general pollution surveys of recent years. It seems clear that fuller value from such surveys could be derived by use of standard techniques permitting cross comparison of findings from center to center. The A.S.T.M. committee in the United States, and such endeavors elsewhere, deserve full encouragement in this work of critical evaluation and standardization.

Air pollution investigations in which effects on health are concerned stand at a difficult stage. Donora perplexes the field with its acute respiratory episode in the presence of subphysiological levels of common irritants. It is evident that advances in knowledge of toxicological safe limits are needed. Of equal importance, however, is basic research on the physico-chemical relationship between particulates and the gases of urban atmospheres. The Los Angeles study, particularly, has shown that an urban atmosphere is a chemical system of diverse and energetic activity. Laboratory studies on the thermodynamics and chemistry of such systems may be the prior requirement in establishing the choice of pollutants which should be estimated in the complex environments on which future study may be undertaken.

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END OF SYMPOSIUM

Catalysis by Anion Exchange Resins

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THE commercial production over the past few years of a steadily increasing number of types of ion exchange resins has stimulated the active investigation of these products as catalysts for organic reactions. The relatively low equivalent weights of the newer resins, combined with their insolubility, offers the possibility of continuous processes with freedom from contaminating ions. The acidic resins have been the subject of numerous studies; the newer, and probably more versatile, basic resins, however, have been used in only a few cases.

Galat (*7*) has reported the hydrolysis of nicotinonitrile to form nicotinamide in the presence of Amberlite IRA-400. Zaslowsky and Astle (*23*) have utilized a variety of anion exchange resins to effect Knoevenagel condensations. Jenny (*9*) studied the mutarotation of glucose catalyzed by anion exchange resins. Ueno (*17*) described the use of anion exchange resins in effecting the aldolization of acetaldehyde and the addition of alcohol to β-propiolactone.

In this work, Amberlite anion exchange resins were employed to catalyze a variety of organic reactions including cyanohydrin formation, benzoin condensation, diacetone alcohol formation, cyanoethylations, and nitro alcohol formation.

Anion exchange resins are effective catalysts for a variety of reactions, particularly those involving low catalyst concentrations and relatively low temperatures, and employing reagents which are not readily hydrolyzed to acids capable of inactivating the catalyst. The relatively high moisture content, thermal instability, and the consequent difficulty of drying the strongly basic quaternary ammonium hydroxide–type resins limit their usefulness. Reactions involving ethyl acrylate and malonic ester in the presence of Amberlite IRA-400 were found to be markedly influenced by the moisture content of the resin.

The catalytic activity of anion exchange resins may be desirable from a preparative standpoint. In many cases involving deionization of reactive organic materials, however, this catalytic activity may be detrimental and must be considered.

In the course of the work on resin catalysis, three different reaction techniques were employed. The first and most frequently used method consisted merely of stirring the reactants with the resin catalyst. This was employed in those cases involving simple condensations such as the addition of alcohol to acrylonitrile and in those cases where relatively long reaction times were necessary. The second method involved passing the mixture of reagents through a jacketed column packed with ion exchange resin. This was employed in those cases where the reaction was