

Aerosol Science and Technology: History and Reviews

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About the Cover

The cover depicts an important episode in aerosol history—the Pasadena experiment and ACHEX. It includes a photograph of three of the key organizers and an illustration of a major concept of atmospheric aerosol particle size distribution. The photograph is from Chapter 8, Figure 1. The front row shows Kenneth Whitby, George Hidy, Sheldon Friedlander, and Peter Mueller; the back row shows Dale Lundgren and Josef Pich. The background figure is from Chapter 9, Figure 13, illustrating the trimodal atmospheric aerosol volume size distribution. This concept has been the basis of atmospheric aerosol research and regulation since the late 1970s.

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Atmospheric Nanoparticles

Early Metrology and Observations (1875–1980)

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Introduction

Contemporary investigation of atmospheric aerosols concerns the origins and nature of very small particles—smaller than $0.1\ \mu\text{m}$ diameter (100 nanometers). Present-day study of these tiny particles, known as nanoparticles, derives from improvements in sampling and analytical instrumentation that have taken place in the past decade. The nanoparticle range has been of great historical interest as well, because nanoparticles are part of the total number concentration of particles that have been observed by various means since the mid-19th century. The nanoparticle size range represents a miniscule size regime of “Aitken nuclei,” from unstable clusters of molecules and ions to stable submicrometer particles capable of further growth. In the early 20th century, scientists built instruments to measure electric charge-mobility (movement of electrically charged particles in an electric field) and determined that ions present in the air had much lower mobility than expected for gases. These ions later were described as small and large ions (Flagan, 1998), identified with the nano-regime, and included in the phenomenology of atmospheric aerosols. Exclusive of the atmosphere, nanoparticles have unusual optical, electrical, diffusional, mechanical, catalytic, and biochemical properties that make them of special interest. Nanoparticles are small enough to be in a transition regime between bulk material and molecular clusters representing very high microsurface exposure that have long been of interest in fundamental colloidal chemistry and microtechnology (Hidy & Brock, 1970).

Over the years, the nomenclature describing particles in different size ranges has evolved. For this chapter, the mid-1960s definitions, superimposed with later descriptions, are a useful starting point. Junge (1952, 1955) described these definitions for the aerosol number-size distribution, as shown

in Figure 1. A current definition of nanoparticles is superimposed on the figure. Particle numbers in the nano range are inferred from instruments used to measure the total number concentrations of particles (N), including Aitken or condensation nuclei (CN), large ions, and Langevin ions (Langevin, 1905). Larger particles, such as ultralarge ions and large and giant nuclei, including cloud condensation nuclei (CCN), are generally present in the atmosphere at much smaller concentrations than the nanoparticles.

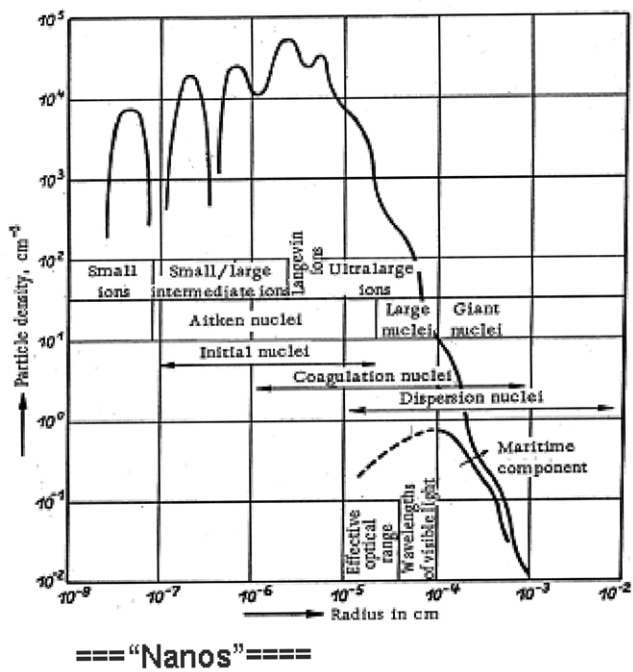


Figure 1. Schematic diagram of nomenclature for regimes of aerosol particle size versus number concentration increment.

Note: Superimposed on this diagram is the nominal range currently considered as nanoparticles (10^{-8} to 10^{-5} cm). Junge believed the gaps in the ion range were real, though we now know that the nanoparticle size range appears to be continuous to molecular cluster sizes ~ 1 nm. Knowledge of the number-size distribution indicates that measurement of the total number of particles (N) is a very good approximation for nanoparticle concentration. The nanoparticle concentration is readily deduced from the shape of the distribution curve, which shows a sharp decline in particle density for particles larger than 10^{-5} cm. Source: Adapted from Junge (1952).

Although observations of airborne particles have been documented through casual study of optical effects for centuries (e.g., DaVinci, noted by Went, 1960), perhaps Coulier (1875) first reported observations of total nuclei concentration, using a primitive vapor-expansion device. A decade later, the English physicist John Aitken (1887/1888) became interested in atmospheric particles. He began systematic observations of the number concentration of CN (assumed as N) using a portable adiabatic expansion chamber that produced water vapor supersaturation, in which nucleated droplets could grow to an optically detectable size. Aitken's instrument formed the basis for CN detectors for decades.

A succession of research beyond Aitken's time, especially in the post-World War II years, determined that clouds in the atmosphere were created through the nucleation and growth of particles $>0.5\ \mu\text{m}$ diameter at water vapor supersaturations of a few percent greater than saturation, far lower than generally achieved in vapor-expansion counters. The total number concentration of particles (N) present in the air is far larger than those particles (CCN) involved in cloud formation. Nevertheless, interest in very small particles has persisted as part of atmospheric chemistry and atmospheric electricity. Tracing the concentrations of CN has provided insight into spatial exchange mechanisms in atmospheric dynamics; they also have important practical applications in air pollution.

Paralleling the development of instruments that employed a vapor supersaturation measuring CN, the atmospheric ion detectors came into use. Initially scientists were interested in gaseous ions observed in electrical condenser mobility analyzers. However, observations offered by investigators such as Langevin (1905) suggested the presence of ions with mobility three orders of magnitude less than gases in the laboratory. The aspiration condenser of McClelland (1898) and Zeleny (1900) was used extensively to measure the mobility of atmospheric ions for more than 20 years.

With the advent of the differential mobility analyzers in the 1920s, researchers made additional observations, giving some understanding of the classification of large and small ions. A differential instrument was reintroduced in the 1950s with Junge's work, which began to clarify the presence of nano- or ultrafine particles as part of the tropospheric particle size distribution (Junge, 1963). Later, in the 1960s, Whitby and his colleagues at the University of Minnesota (Whitby & Clark, 1966) refined an earlier differential mobility analyzer design and coupled the new instrument with

a CN counter and an optical counter to obtain continuous observations of particle size distributions in many locations.

The direct measurement of nanoparticles as a function of size proved to be very difficult with methods available prior to the 1970s. To some degree, the diffusion battery (Nolan & Guerrini, 1935) offered opportunities for such observations; however, these devices were difficult to use for size-differentiated nanoparticle studies because of the limited means available for particle size determinations.

The metrology of nanoparticles represents an unusually rich topic in the history of atmospheric aerosols. The purpose of this chapter is to present a brief review of the variety of instruments adopted for nuclei measurement and to illustrate the results of observations achieved into the 1970s, especially in relation to cloud microphysics and air pollution. Some interesting applications of the method are included to indicate the technological ingenuity of the users of the method.

Measurement Principles

Design of instrumentation for measuring nanoparticle concentrations relies on three fundamental, size-dependent principles: (a) nucleation or growth by condensation of supersaturated vapor, (b) diffusion of particles by Brownian motion, and (c) electrically charged particle mobility induced by electrical forces.

Vapor Supersaturation

Supersaturation is achieved by cooling during expansion of a moist gas or by vapor transfer between a warm, wet surface and a nearby cool surface. Production of particles as a condensate fog at a given supersaturation depends on the absence or presence of “centers for condensation,” or nuclei. If no nuclei are present, nucleation and condensation take place at high vapor supersaturation by homogeneous processes. If nuclei are present, such as ions or visually nondetectable particles, the supersaturation required is lower, and the vapor condenses on the existing particles. Nucleation and growth in water vapor are dependent not only on particle size but on their physicochemical properties, including solubility (Mason, 1957a; Fletcher, 1966).

The supersaturation ratio (S) for the expansion devices can be estimated readily from the ideal gas law; the percent supersaturation is given as

$$100(S - 1), \text{ where } S = p/p_{\infty} = p_1/p_2 (V_1/V_2)^{\gamma}, \quad (1)$$

where p_{∞} is the saturation vapor pressure of the fluid. The volume V_1 is the volume before expansion, and V_2 is the volume after expansion; p_1 is the saturation vapor pressure of the fluid at temperature T_1 before expansion, and p_2 is that at temperature T_2 after expansion. The exponent γ is the ratio of the specific heats of the vapor at constant pressure and constant volume. The relation between the supersaturation ratio and the expansion ratio is nonlinear; supersaturations of a few percent are generally sufficient to activate natural occurring CN, except for small ions and particles with very large fluid contact angles with a solid nucleus.

Vapor supersaturation also can be achieved by passing air through a volume with the upper and lower plates saturated with water at different temperatures (T_1 and T_2). Supersaturation is reached in mid-chamber as a result of mass and heat transfer across the plates. The condensable vapor is distributed by diffusion, and provided there is no heat loss to the side walls, the fluid vapor pressure in the air will be linearly related to the temperature. Because the saturation vapor pressure is not linearly related to its temperature, the diffusional mixing leads to a supersaturated condition in the chamber. The vapor in the chamber must be at p and T lying between the conditions of the two wet plates. The equilibrium vapor pressure of the fluid at temperature T is however p' , so that the supersaturation is $(p - p')/p'$. This ratio has a maximum near the temperature $(T_2 - T_1)/2$. If there is stirring in the chamber, all particles should experience a supersaturation equivalent to a maximum during their residence in the chamber.

Counters using the diffusion principle have an advantage over the expansion devices because the supersaturation tends to be constant until appreciable particle growth is achieved. However, high supersaturation is difficult to achieve, but values in the range of 0.1% to 3% can be obtained—a regime for which it is difficult to design with expansion instruments. A serious drawback to the diffusion chambers is the influence of the side walls. If they become cooler than the vapor, then larger supersaturation may occur along these walls, upsetting the measurements.

Once supersaturation is achieved in the vapor, nucleation can take place on existing airborne ions or particles, or in some circumstances by self- or

homogeneous nucleation. Macroscopic theory of nucleation basically depends on estimating a rate of production of particles, which is a function of the vapor-supersaturation-extending equilibrium models. At equilibrium, the vapor pressure $p_s(r)$ of condensable vapor over the surface of a droplet of radius r exceeds pressure $p_s(\infty)$ over a plane water surface at the same temperature, as expressed by the Kelvin equation (Mason, 1957a). For a pure liquid, this is as follows:

$$p_s(r)/p_s(\infty) = \exp (\{2\sigma\}/\{\rho_w R_v T r\}) = \exp (k/r), \quad (2)$$

where

r = droplet radius,

$p_s(r)$ = saturation vapor pressure of a droplet of size r ,

$p_s(\infty)$ = saturation vapor pressure over a bulk surface of water,

σ = surface tension,

ρ_w = water density,

$R_v = \frac{R}{M_w}$ = gas constant of the condensable vapor,

M_w = mole weight of water,

R = universal gas constant,

T = temperature °K, and

$k = \frac{2\sigma}{\rho_w R_v} = \frac{3.3 \cdot 10^{-5}}{T}$.

Thus, a droplet introduced into a just-saturated atmosphere will evaporate; a droplet cannot persist, much less grow, unless the environment is supersaturated by the amount required by the Kelvin relationship. A critical radius can be defined for a droplet to be at equilibrium with its vapor. Table 1 gives critical radii for pure water as an example. One can readily see the dramatic difference in droplet size with the increased supersaturation ratio from these calculations.

Table 1. Critical radii for water droplets at 20°C for different supersaturation ratios calculated from the Kelvin model

Supersaturation Ratio	Critical Radius, r^* (nm)	Number of Molecules in the Nucleus
1.01	120	2.5×10^8
1.1	12.6	2.8×10^5
2.0	1.73	730
10	0.52	20

Note: Realization of a high supersaturation would activate a range of particles of different size. Landsberg (1938) discussed supersaturation calculations, including probability distributions for homogeneous nucleation.

If a droplet is formed on a wholly or partially soluble nucleus, the equilibrium vapor pressure at its surface is reduced by an amount depending on the nature and concentration of the solute, which means that condensation will occur at a lower supersaturation than on an insoluble particle of the same size. This behavior is governed by Köhler's (1921, 1926) vapor pressure ratio to solubility relationship for critical droplet size. This relationship was modified somewhat later by Mason (1957a). A condensation nucleus is said to be activated when the droplet formed around it reaches r^* , given by the Kelvin-Köhler relationships. Once the droplet exceeds this size, it will continue to grow to cloud droplet size if the ambient saturation ratio remains at a value above the equilibrium curve.

Junge (1935) used the Köhler equation to calculate r^* as a function of solute concentration (e.g., pure water versus a sulfuric acid nucleus) and temperature. Sulfuric acid was assumed as a surrogate for a seed nucleus for CN production. As an example, a sulfuric acid nuclei of 10 nm (10^{-6} cm) in diameter would require a 5% supersaturation to be activated. However, in many cases the chemical composition of a CN is unknown. In the theory of nucleation and formation of CN, one of the persistent questions concerns the lowest size r^* at which they are activated by the applied supersaturation.

Because the classical equilibrium theory for nucleation or growth of pure compounds or soluble mixtures was worked out in the 1930s, the theory has become increasingly complex and has involved considerations of multicomponent solutions, surface properties, and molecular clusters for the nano-size range. However, the classical thermodynamics model is sufficient for characterizing the principles of nucleation, as seen in the CN counters.

Brownian Diffusion

Scientists observed thermal agitation of tiny particles in the nano-range in liquids early in the 19th century. In analogy to diffusion in gases, small particles can “diffuse” through concentration gradients. Later, Einstein (1905) theorized that this motion is inversely proportional to particle size but principally affected the nano-range, because inertial forces on particles are important for larger particle motion. Diffusion of particles by Brownian motion has been observed since the 19th century, but Einstein worked out the theory for such motion shortly after the turn of the 20th century. Basically, the thermal motion of particles is described through a diffusion coefficient,

$$D = BkT, \quad (3)$$

where T is the absolute temperature, k is the Boltzmann constant, and B is the particle mobility, given by Einstein’s theory as $1/6\pi\eta r$, where η is the viscosity of the suspending gas. For very small particles, an added multiplier is the Stokes-Cunningham correction for gas “slip” around the particle. In analogy to gaseous diffusion, Brownian diffusion to a surface is given in terms of a flux proportional to particle concentration gradient (Hidy & Brock, 1970).

Using the particle mobility, a device could be constructed to trap flowing particles as a function of size on a surface. With suitable detection with distance, such devices, called diffusion batteries, appeared in the 1920s (Nolan & Guerrini, 1935).

The theory for particle deposition by diffusion in a slow-moving aerosol was developed before 1940, as reviewed by Knutson (1999) and others. For example, in an appendix to a paper by Nolan and Nolan (1938), Gormley derived the expression for the fraction of particles of diffusion coefficient D penetrating the channel of length L , half height b , and width a with a gas flow rate of q .

$$F = 0.910 \exp(-x) + 0.053 \exp(-11.4x), \quad (4)$$

$$\text{where } x = \frac{3.77bDL}{aq}.$$

The theory of the diffusion battery is thus well established, and the use of such a battery presents an attractive and convenient method of determining the diffusion coefficients of submicrometer particles and subsequently their effective “mean” size and size distribution from the variation in penetration of particles through the battery.

Electrical Forces

Measurement of ions and conductivity in the atmosphere's electrical field has been used to infer nanoparticle concentrations (Ebert, 1901; Israel & Schultz, 1932; Junge, 1963; Reiter, 1985; Flagan, 1998). Particles carrying electrostatic charge move at different rates in an electric field, depending on particle size and charge. Scientists applied this principle to measure ions present in the air.

Electrical mobility analyzers depend on the detection of a collected charged particle, in analogy to a diffusion battery. Millikan (1917) showed that small particles carrying an electrical charge move in a gas under an electrical field E . Instead of relying on particle diffusion to a surface, electrical mobility depends on the action of an external force on the particle to induce motion toward a surface. Electrical mobility Z for a charged particle is given as

$$Z = v/E = neB, \quad (5)$$

where v is the cross-stream particle velocity, E is the electric field strength, and n is the number of unit charges (e) on the particle. Using a suitable electric charge detector, the presence of a particle of given size can be counted, because Z is inversely proportional to particle diameter.

As a rough analogy to Gormley's relationship for a diffusion battery, a relationship between a charged-particle mobility spectrum and the second derivative of the current-voltage in an instrument with cylindrical geometry is given as

$$dN/dZ = (d^2i / dE^2) \times 2LE^2 / [\pi e^2 v^2 (b^2 - a^2) 2 \ln(b/a)], \quad (6)$$

where dN = number of ions/cm³ in the mobility range between mobility Z and $Z + dZ$, L = length of the electrode, E = condenser voltage, v = average velocity of the ion, b and a = radii of the outer and the inner electrode, respectively, and i = ion current. This equation represents the basis for the experimental determination of the mobility values by observing the breakpoints of the current-voltage characteristics in a cylindrical condenser.

Evolution of Instrumentation

Vapor Condensation

Instruments to detect nuclei are readily designed to produce vapor supersaturation in analogy to atmospheric processes. Nuclei then can be detected optically after rapid condensation growth in a supersaturated vapor

(Podzimek, 1989; McMurry, 2000a). The first experiments to demonstrate condensation of water vapor on nuclei were reported by Coulier (1875) and Aitken (1890/1891), who showed that a fog formed by expansion (adiabatic cooling) in supersaturated air was made denser on introducing combustion products. Aitken concluded that when water vapor condensed in the atmosphere, it always did so upon the dust particles present, using the term “dust” in a wider sense to include hygroscopic and nonhygroscopic particles of all sizes. He was also able to show that the nuclei were not equally effective. Condensation occurs on some with expansion ratios of less than 1%, whereas others required very large expansions of a few hundred percent. Aitken constructed various forms of his dust- (or condensation) nucleus-counter for measuring the number of aerosol particles per unit volume, one of which is shown in Figure 2, along with a later design of Scholz (1932) in Figure 3.

In today's terminology, the Aitken and Scholz designs are water-based, noncontinuous- expansion-type instruments, with single droplet counting. Sufficient supersaturation (typically 200% to 350%) was achieved by rapid adiabatic expansion. Under these conditions, homogeneous or nanoparticle-based nucleation may take place on “nuclei” as centers for condensation, growing into an easily visible droplet. Particle concentrations then could be calculated by visually counting the droplets after they precipitated onto a microscope counting graticule.

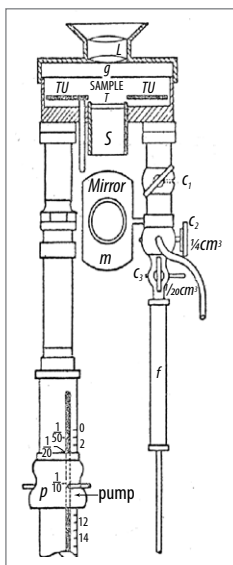
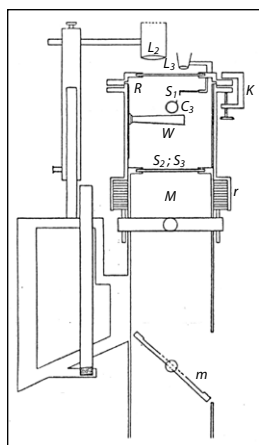


Figure 2. Aitken counter (far left) and schematic diagram of the counter (left).

Note: The replica of the Aitken counter was manufactured by Casella Ltd., London. The central receiver (expansion chamber), r , is lined with wet blotting paper for near supersaturation; p is a piston to introduce air samples into r for vapor rarefaction and condensation; c_1 to c_3 are cocks for outside air or to a cotton wool filter, f ; and l (lens), g (glass), and m (mirror for light transmission) are the optical system for nuclei counts.

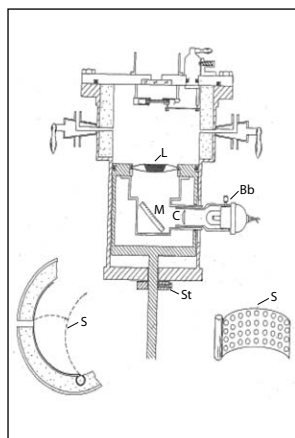
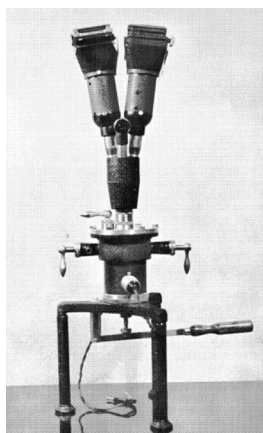
Photo: Courtesy of the author; schematic diagram from Landsberg (1938).



Note: This instrument was manufactured by Schulze, Potsdam. It was brought over from Germany in 1934 by Landsberg and eventually given to Woods Hole Oceanographic Institution. *R* is the receiver (expansion chamber) lined with wet blotting paper, *W* is a wetted cotton wool filter to equalize pressure in *R*, and *C₃* is the cock for injecting air into *R*. The optical system includes lenses *L₂* and *L₃* for viewing the reticulated glass plates *S₁*, *S₂*, and *S₃*, with light from the mirror, *m*. *M* is an open cylinder, and *r* is leather ring seals. Photo: Courtesy of the author; schematic diagram from Landsberg (1938).

Figure 3. Modified Aitken counter design of Scholz (left) and schematic of the receiver section (right).

A stereoscopic viewing, photographic version of the Pollak counter, designed by Pollak and Daly (1958), is shown in Figure 4. Visual counting was replaced by photographing the droplets formed after expansion (Pollak, 1952; Pollak & Daly, 1958). These instruments are called absolute nucleus counters because they require only calibration using a fixed geometry in the optical microscope graticule. A considerable operational improvement



Note: The dark-field illuminator in the lower section below the expansion chamber is accommodated in the piston of the expansion pump and moves with the piston. The illuminator consists of a lens, *L*, blackened in the center; a mirror, *M*; and an electric bulb, *Bb*, with a condenser lens, *C*. (Prolonged and uninterrupted use of this counter was found not to produce fogging of the graticule—a deficiency of earlier counters.) Source: Pollak and Daly (1958).

Figure 4. The Pollak and Daly condensation nuclei counter with stereo-photomicrographic recording (left) and schematic of the receiver section (right).

of these manual counters was reported by Bradbury and Meuron (1938), who developed a photoelectric nucleus counter. Their instrument sensed photoelectrically the attenuation of a light beam by the droplets formed on the nuclei rather than actually counting the number of drops.

Nolan and Pollak (1946) constructed two models of photoelectric counters, the direct-beam photoelectric nucleus counter and the multiflex photoelectric nucleus counter. A photograph of Nolan and Pollak, with T. A. Rich, is included as Figure 5. Subsequent improvements (Pollak & O'Connor, 1955) led to the final Pollak Model 1957 built by Pollak and Metnieks (1957), as shown in Figure 6. Improvements in the photoelectric counter included reducing the diameter of the fog tube to 1 inch and changing the illumination through this tube to a slightly convergent beam. This instrument became the reference for many CN networks and was manufactured until the early 1980s by Robert Gussman (BGI) of Waltham, Massachusetts. Four replicas of the Pollak counter manufactured by BGI were used by the National Oceanic and Atmospheric Administration at Mauna Loa, Samoa, and the South Pole. A recalibration of these instruments after 20 years showed a response curve to be unchanged.

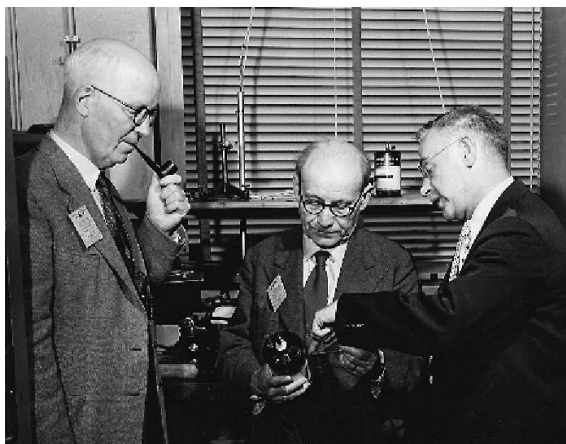


Figure 5. Prof. Pollak (center) and Prof. Nolan (left) with Dr. T. A. Rich (right) at the General Electric laboratories, Schenectady, New York.

Photo: Courtesy of the author.

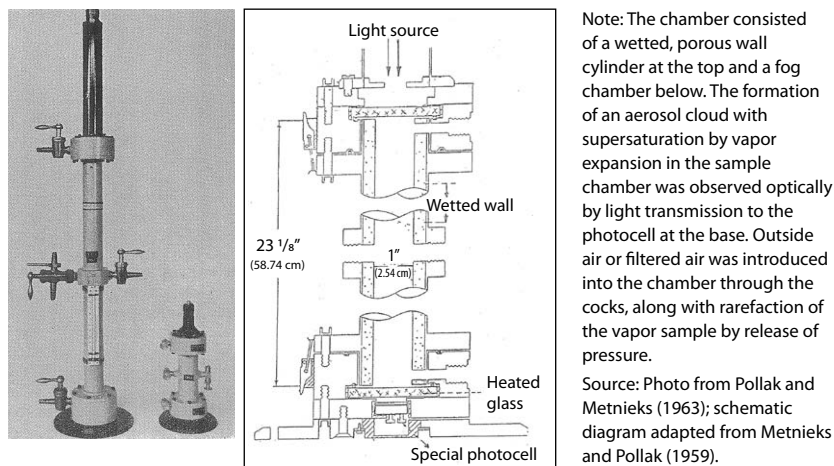


Figure 6. Photoelectric condensation nuclei counter (Pollak Model 1957) and small, portable photoelectric condensation nuclei counter (left) and diagram of the receiving chamber of the counter (right).

Photoelectric counters are relative instruments and were calibrated against some reference, such as an Aitken counter. The calibration of the Pollak counter was done by a tube-bridge dilution system that produced a response curve for the instrument. The response curve was fitted to absolute values at several points by using simultaneous measurements with a photographic version of an expansion-type counter. The Pollak and Metnieks (1960) calibration of the photoelectric nucleus counter is within 10% of that obtained by comparison with several “absolute” nucleus counters and also when compared with independent, nondroplet-forming aerosol techniques (Liu et al., 1975). Using a slide placed between the photocell and the fog tube, William Winters developed a simple field optical calibration of the Pollak counters. The slide contained an open window, three neutral density filters, and an opaque window. Winters set the instrument at full scale on the open window and simulated an expansion by sliding a neutral density filter in place. Loss of transmission equal to that of the filter verified that the optical and electrical components were responding properly.

Vonnegut (1949, 1954) designed the first fully automated and continuously operating, water-based, expansion-type photoelectric CN counter, with improvements added later by Rich (1961). The air was bubbled through water to humidify it, and a cloud was formed in a small chamber by a

pulsating pressure from a diaphragm pump. The density of the cloud was measured by the forward scattered light in a dark illuminator. This instrument was used on aircraft searching for submarines (combustion aerosol from submarine diesel engines). Skala (1963) developed the General Electric (GE) condensation nuclei meter, as shown in Figure 7. Skala adopted many of the Rich (1961) design features and developed the first commercially available “automatic” photoelectric instrument, with five expansion cycles per second and a concentration range from 300 to more than 10^7 particles/cm³. Upon founding the Environment One Company in 1972, Skala and Rich developed a new automatic CN counter, which they marketed commercially as the E/One Rich 100 and 200 instruments.

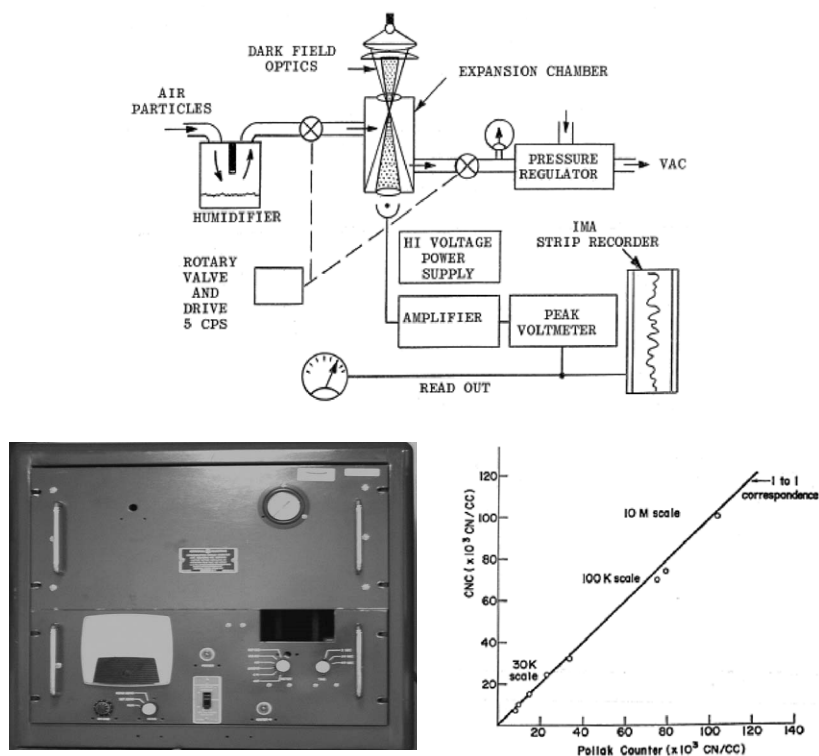


Figure 7. General Electric continuous condensation nuclei counter.

Note: The counter involves expansion and compression with a continuous air sampling and exhaust through a rotary diaphragm valve and photoelectric detection of the onset of nucleation. At the top is a schematic of the instrument. Lower left is a photo of the front face of the instrument, and the calibration curve for the counter versus the Pollak counter reference is at the lower right.

Photo: Courtesy of the author; schematic diagram and calibration adapted from Skala (1963).

Virtually all research and CN monitoring before the mid-1970s used expansion-type instruments, with water as the working fluid. Since then, expansion-type CN counters were increasingly replaced by vapor-diffusion-based CN counters, where the condensation growth is achieved by forced convection. Early on, Langsdorf (1936) built a vapor-diffusion-based CN counter using methyl alcohol as a working fluid. Rosen designed the first continuous particle counters (CPCs) of this kind during the 1970s (Rosen et al., 1974; Bricard et al., 1976; Sinclair & Hoopes, 1975). Rosen's instrument was a thermal-gradient diffusion cloud chamber using water as the condensing species. The Bricard and Sinclair and Hoopes instruments used a warm saturator followed by a cold condenser where the growth started. These two instruments employed alcohols as the condensing vapor. Alcohols were used mainly because their vapor pressure is high enough that particles grow to detectable sizes and their diffusivity is low enough to prevent the vapor from diffusing too fast to the walls of the instrument. Agarwal and Sem (1980) described a later model.

Another type of steady-flow instrument is the mixing-type CPC. In these instruments, cold aerosol flow is turbulently mixed with hot vapor and then cooled rapidly. Typical working fluids are water and different oily substances, such as dioctyl-phthalate. Sutugin and Fuchs (1965) built the first of these instruments in Russia. The advantages of these instruments are that they can be designed easily to have small diffusional losses and small detectable sizes. They can also handle large sample flow rates. The steady-flow instruments have grown in favor because of the ease with which absolute concentrations can be measured using single particle counting techniques and because the steady flow eliminates pulsations that can interfere with associated instrumentation, such as differential mobility analyzers or diffusion batteries.

The Diffusion Battery

In the early 20th century, samplers based on diffusion of particles in Brownian motion emerged that have been useful for detecting nano-range particles. Nolan and Guerrini (1935) initially applied the method to CN by using a diffusion battery containing a number of parallel rectangular channels. Diffusion batteries based on Brownian diffusion in laminar flow have been designed and used for particle number-size estimates (Thomas, 1955; Fuchs & Stechkina, 1962) or have been used with supersaturators for size-differentiated nuclei counting (Pedder, 1971). A variety of designs for diffusion batteries

were developed (Knutson, 1999) and applied to atmospheric nanoparticle sampling (Twomey & Severynse, 1964). After the 1970s, the use of diffusion batteries was supplanted by continuous methods, such as the electrical mobility analyzer, and the diffusion batteries were largely abandoned for atmospheric observations.

The usefulness of diffusion batteries was significantly enhanced when Pollak and Metnieks (1957) showed that, through application of a mathematical algorithm, called data inversion, these devices could be used to determine aerosol size distributions, not just the mean particle size. Knutson (1999) also noted that D. Sinclair simplified the inversion problem by using a graphical stripping technique for a polydispersed aerosol to obtain a size distribution. Fuchs and Stechkina (1962) and a number of other investigators refined the data inversion theory, extending into the 1990s (Knutson, 1999).

Rich (1966) developed an example of a combination of the diffusion battery concept and an electrical detector. He described a parallel-plate device with electrically isolated metal plates. With the plates at the same potential, the sampler functioned as a diffusion battery. With 300 volts applied to alternate plates, it could be used to measure not only the particle diffusion losses but also the fraction of particles charged. If readings were taken of an aerosol fed directly to a CN counter, after passing through the diffusion battery with no voltage applied and with voltage applied, then two component aerosol particle models could be determined. This process would characterize the unknown aerosol being measured, providing the mean diffusion coefficient (diffusion size) and the mean electrical mobility of the aerosol.

Ion Mobility Analyzers

The application of electrical mobility to atmospheric particle measurements occurred roughly a decade after Aitken's work. The coaxial condenser mobility analyzer (integral method), introduced by McClelland (1898) and improved by Zeleny (1900), enabled Ebert (1901) to measure atmospheric ions as early as 1901. Other observations of atmospheric ions date back to Langevin (1905), McClelland and Kennedy (1912), and Pollock (1909, 1915). A broad range of electrical mobility observations were made from small ions with mobility of about $1 \text{ cm}^2/\text{volt sec}$ and an estimated size of a few tenths of nm to ultralarge ions with mobility of about $10^{-4} \text{ cm}^2/\text{volt}$ and estimated sizes of well over 100 nm (Nolan et al., 1925). Torreson and Wait (1934), as well as others, showed that the large ions are related to the neutral CN in the

atmosphere, their only difference being the acquisition of a charge through collision with small ions of either sign (bipolar ion charging).

Scientists obtained small ion and nanoparticle mobility spectra in the diameter range of 0.4 nm to around 15 nm from instruments derived from the ventilated cylindrical capacitor designs of Zeleny (1900) and Gerdien (1905). The distinction between small ions and nanoparticles was defined by mobility, with particles of mobility greater than $5 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (smaller than $\sim 1.8 \text{ nm}$) classified as small ions and particles of lesser mobility (larger size) classified as nanoparticles. Mobility, mass, and diameter are evaluated by application of kinetic theory (Chapman & Cowling, 1960), which can include the effects of direct coulomb interaction, image charge interaction, and a Lennard-Jones interatomic potential.

The aspiration condenser, which used a cumulative estimate of electrical mobility from equation 6, dominated measurements of atmospheric ions until the late 1960s, even though Erikson (1921) previously developed a differential mobility analyzer. The differential method of determining mobility has the advantage over the integral method of directly giving the percentage of particles with mobility lying in a given range. The current flowing to the electrode is so small, however, that it is difficult to measure. After the electronics were improved in the 1960s, these instruments were reintroduced. They were based on condenser measurements of atmospheric ions, which Junge (1955) used to describe the structure of the nanoparticle number-size distribution (Figure 1).

In the 1960s, Whitby and his colleagues at the University of Minnesota developed an electrical mobility analyzer, which is the basic prototype used today for a range of nanoparticle size determinations. The electrical mobility analyzer was a refinement of earlier developments, including a Faraday cup electrometer used earlier by Zeleny and McClelland. The instrument with electrical charge detection associated with particle mobility represented an important breakthrough for continuous observations of particle size distributions in the nano-range. Whitby and Clark (1966) incorporated a sensitive micro-microammeter into their differential mobility analyzer design. This 1960s Keithley electrometer avoided the delicate electronics of earlier detectors and was more robust for field use. The sensitivity of their mobility analyzer with the Keithley electrometer was determined to be 10^{-13} amperes or 10^6 electrons/sec. The minimum charged particle concentration that could be measured was $\sim 1,000/\text{cm}^3$ with an aerosol flow of 1 liter/sec. Thus, without

further refinement, the mobility analyzer could measure urban nanoparticle levels but not offshore marine or upper tropospheric conditions.

The concept of the Whitby mobility analyzer for segregating polydispersed aerosols is shown in Figure 8. This instrument depends on controlled charging of particles as a function of size, followed by lamellar flow of the charged aerosol through an annulus such that the smallest particles migrate to a central annular electrode or to the tube walls in an electric field across the tube. Larger particles deposit farther down the annulus. The radial velocity is determined by a balance between the electrical force field and the opposing drag force on the particles. Those particles that are not collected on the electrode at a given voltage flow into an electrometer for measurement. By varying the imposed voltage across the outer wall of the tube and the inner electrode, a resulting particle flow to the electrometer can determine electrical mobility of a size fraction and thereby deduce particle number-size distributions in the range of ~5 to 500 nm.

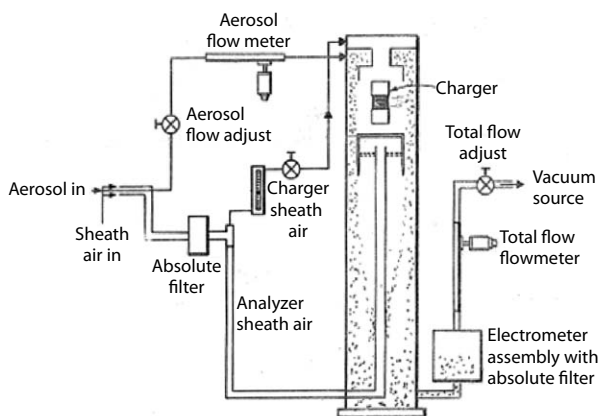


Figure 8. Conceptual scheme for the electrical mobility analyzer.

Note: This analyzer is most effective for particle measurements in the ~5 to 500 nm diameter range and is based on a relationship between unique charge accumulations as a function of particle size.

Source: Adapted from Whitby and Clark (1966).

The electrical mobility analyzer was coupled with a calibrated optical counter for the 500 to 10,000 nm range and a CN counter to provide a means of measuring N and the number-size distribution from the nano-range of ≤ 5 nm to the coarse or giant particle regime of 10,000 nm diameter (Whitby & Sverdrup, 1980). This hybrid, called the Minnesota Aerosol Analyzer System (MAAS), was sufficiently robust and reliable to be commercially produced after the 1970s by TSI, Inc., of Minneapolis, Minnesota. With modern CPCs and fast digital signal processing, the MAAS technology serves as a basis for measuring particle number-size distributions today.

The Whitby electrical mobility analyzer was calibrated in the laboratory using suspended monodispersed particles of a known diameter. This instrument was compared with the Pollak CN counter in the 1970s (Liu et al., 1975). A comparison between the two instruments is shown in Figure 9. These experiments showed conclusively that the Pollak water-based CN counter is indeed an aerosol particle detector, and its response is unaffected by the size and the chemical constituency of the particles with the range of conditions covered by these experiments. Thus, the Pollak instrument and associated CN devices are capable of measuring particle number concentration comparable with alternate methods.

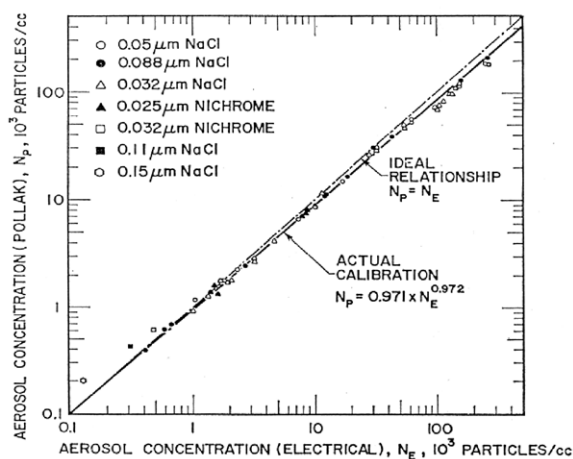


Figure 9. Water-based expansion counter (Pollak Model 1957) versus electrical mobility analyzer of the University of Minnesota for monodispersed aerosol particles of NaCl and Nichrome.

Source: Liu et al. (1975). Reprinted by permission of the American Meteorological Society.

Nuclei Observations in the Atmosphere

The discovery of nanoparticles in the atmosphere in 1875 triggered intense scientific interest as to their origin, chemical constitution, and global distribution. Early on, scientists postulated that all radiations originating beyond the earth's atmosphere, in particular, the ultraviolet radiation, as well as radioactive gases emanating from the soil and other ionizing radiation (e.g., X-rays and electrical discharges), potentially initiate the creation of nuclei if the proper precursor gases are present in sufficient quantity (Aitken, in Knott, 1923). Researchers investigated a host of substances for their nucleation potential, and human activities, especially combustion of all kinds of material, came under scrutiny. Even the passage of the earth through the tail of Halley's Comet in 1910 was watched for increase of nuclei, but nothing abnormal could be found (Aitken, 1910; Tetens, 1911). Some hundred years after their discovery, a rather broad knowledge base as to the presence of CN in the earth's atmosphere has accumulated. An understanding of the physicochemical processes and mechanisms involved in homogeneous and heterogeneous particle formation now exists.

Using the early counters in parallel with other aerosol particle sampling, scientists reported a variety of observations, beginning with Aitken's work. Thousands of observations of early CN concentrations across the world were summarized before World War II for different conditions in the troposphere, as listed in Table 2. The table indicates that the nuclei concentrations vary widely, depending on the remoteness of the location and in marine or continental conditions. It appears that the lowest concentrations typically fall in the 10^2 to 10^3 nuclei/cm³ range, whereas in polluted air concentrations exceeding 10^4 to 10^6 nuclei/cm³ can be found. These ranges suggest that aerosol particles are present from sources or from atmospheric formation under virtually all conditions. The CN data also show a strong contrast between rural and urban conditions—an early measure of air pollution.

Representative CN concentrations over the oceans, remote from human activity and not modulated by local variations in topography and terrain, were first reported from the research ship *Carnegie* on her various cruises. Before the *Carnegie* voyage, researchers reported a number of atmospheric conductivity observations, which evidently were unadjusted for CN concentrations. Observations from 221 locations indicated that concentrations less than 40×10^2 nuclei/cm³ comprise more than two-thirds of all the observations (Shiratori, 1934). Scientists aboard the *Carnegie* also

measured electrical conductivity of the atmosphere (air-earth current) during the ship's voyages. The observed levels of conductivity depended on the N concentration, because small ions are annihilated rapidly by particle collisions and thereby reduce the conductivity. The sources of particles in the remote marine atmosphere were largely attributed to evaporated sea spray.

Table 2. Summary of Aitken nuclei (CN) concentration ranges in the troposphere in different geographical conditions (observations in 10^3 nuclei/cm³)

Locality	Places	Observations	Average	Avg. of Maxima	Avg. of Minima	Absolute Maximum	Absolute Minimum
City	28	2,500	147	397	49.1	4,000	3.5
Town	15	4,700	34.3	114	5.9	400	0.620
Country inland	25	3,500	9.5	66.5	1.05	336	0.180
Country seashore	21	2,700	9.5	33.4	1.56	150	0
Mountain 0.5 to 1.0 km altitude	13	870	6.0	36.0	1.39	155	0.03
1 km	16	1,000	2.13	9.8	0.450	37	0
>2 km	25	190	21	5.3	0.160	27	0.006
Islands	7	480	9.2	43.6	0.460	109	0.08
Oceans	21	600	0.941	4.68	0.840	39.8	0.002

Source: Landsberg (1938).

Several decades later, the State University of New York at Albany created a network for CN measurements. This program measured the geographic distribution of CN over the North Atlantic Ocean with the participation of the State University Maritime College and many of its alumni, who made observations from ships. The US Merchant Marine also contributed to the project. Merchant ships frequently crossed the ocean on fixed routes, providing opportunities for repeated measurements by location (Hogan et al., 1967). An analysis of the average value of CN concentrations recorded with specially modified and calibrated photoelectric counters is shown in Figure 10 for the time period 1966 to 1971 (Hogan et al., 1973). On average, a strong continental influence was observed well west of Europe and east of North America and in the Bermuda and Azores high barometric-pressure

regions. These continentally influenced CN concentrations were often found to extend across the Atlantic Ocean at 40°N in fair weather. In contrast, during stormy conditions, concentrations $<3 \times 10^2$ nuclei/cm³ were often found a few kilometers offshore. A chronology of mid-Atlantic CN data shown in Figure 11 from different investigators does not reveal an obvious long-term trend.

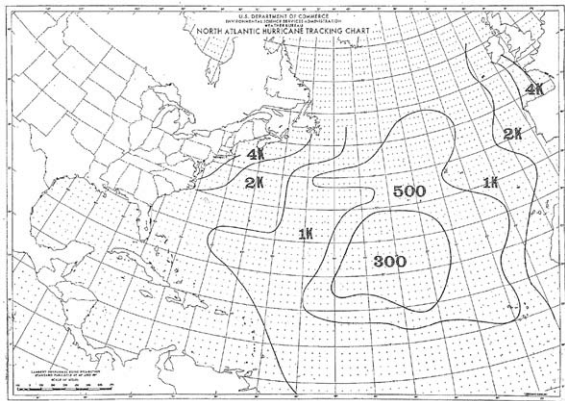


Figure 10. Mean condensation nuclei concentrations (nuclei/cm³) observed over the North Atlantic Ocean during the period 1966–1971.

Note: The highest mean values were found in the regions generally characterized by persistent high-pressure systems. The lowest concentrations were found in mid-ocean. The large-scale gradients in condensation nuclei (CN) imply long-range transport of CN with near-surface air flow from the continents, which was well established in the 1980s. Source: Hogan et al. (1973). Reprinted by permission of the American Meteorological Society.

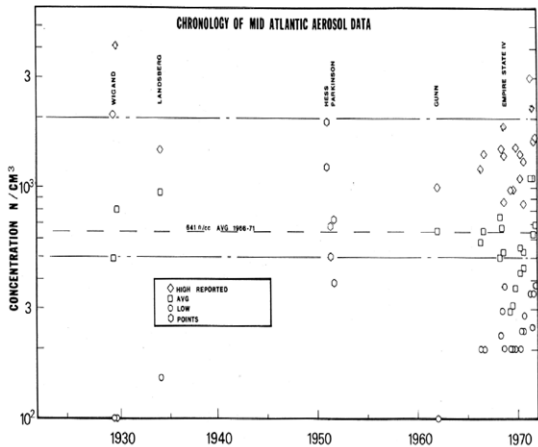


Figure 11. Measurements of marine condensation nuclei concentrations (nuclei/cm³).

Note: The graph includes data from Wigand (1929), Landsberg (1934), Hess and Parkinson (1952), Gunn (1964), and Hogan and colleagues (1973) (Empire State, 1966–1971). Data show a large scatter, but no evidence of trends from the 1930s to 1970, even though Gunn (1964) suggests a few percent increase in fine particle concentrations between 1929 and 1962. Source: Data collected by Hogan et al. (1973)

Early in the 1900s, Wigand (1919) explored the vertical distribution of CN in the troposphere. Much later, Junge (1961; Junge et al., 1961) combined his results with earlier results in conjunction with developing a description of particle concentrations in the troposphere and the lower stratosphere. A composite of these observations is shown in Figure 12. The CN concentrations generally decrease with altitude to levels well below 10^2 particle/cm³, as Junge demonstrated. Included in Figure 12 is an altitude profile obtained over Sioux Falls, South Dakota, in June 1960 with a specially designed, balloon-borne, expansion-type counter with photographic recording (Junge, 1961). The instrument measured all particles below 100 nm and concentrations between 1 and 500 particles/cm³. Junge's investigation eventually led to the discovery of the stratospheric aerosol layer around 20 km altitude, called the Junge layer in his honor (Junge et al., 1961). The average distribution shown in the troposphere from Junge's composite below about 12 km can be interpreted in terms of the vertical mixing of a ground-based, "global" particle source (Hidy, 1972).

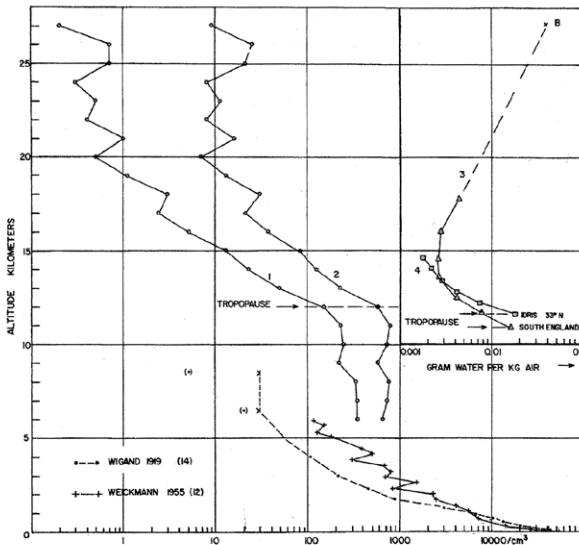


Figure 12.
Observations of the
vertical distribution of
condensation nuclei
(nuclei/cm³) based on
Junge's summary.

Note: The increases in concentrations in the lower stratosphere are often associated with Junge's discovery of the sulfate layer at ~25 km. Curves 1 and 2 are from aircraft flights. The two lower curves are based on data of Wigand (1919) and observations of Weickmann (1955). The inset curves are water vapor mixing ratios. The decline in concentration with height can be attributed largely to vertical mixing of a ground-based particle source with atmospheric turbulence (e.g., Hidy, 1972).

Source: Junge (1963).

A group of University of Wyoming scientists (Rosen et al., 1974) obtained regular stratospheric CN profiles by using a thermal-gradient diffusion cloud chamber that dated back to the stratospheric Climatic Impact Assessment Program (CIAP) of the mid-1970s. These profiles, an example of which is shown in Figure 13, have been used as a fundamental measure for the calibration of lidar-based remote sensing of the atmosphere. The sampling aloft continues to be of significant importance as a trend indicator for the CN concentration aloft and for characterizing the stratospheric aerosol.

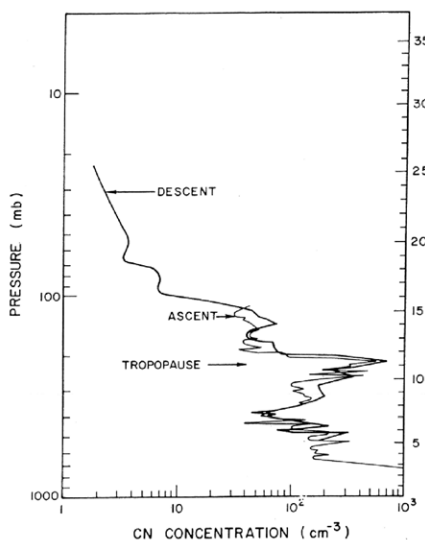


Figure 13. Example altitude profile obtained with the Wyoming condensation nuclei counter (Climatic Impact Assessment Program) thermal-gradient diffusion cloud chamber (working fluid: ethylene glycol).

Source: Rosen et al. (1974).

Hogan and Mohnen (1979) reported an unusual experiment to examine the distribution of CN at all latitudes during a brief period as part of a circumpolar navigation of the earth on October 28–31, 1977, by Pan American Airways Flight 50 in celebration of that airline's 50th year of operation. A Boeing 747SP was used for that flight and carried instruments deployed by the National Aeronautics and Space Administration for its Global Atmospheric Sampling Program (GASP). The 747SP aircraft, cruising at altitudes near the tropopause (as high as 13 km), was equipped with an automatic CN counter specially designed for the GASP program by the Environment One Company. The latitudinal variation in CN concentration around the world from the flight is shown in Figure 14. Concentrations of 10 to 40 nuclei/cm³ were found in

the Arctic and northern mid-latitude stratosphere, and concentrations of 10 to 25 nuclei/cm³ were found in the stratosphere in those latitudes over the Southern Hemisphere. CN concentrations measured in the tropical troposphere are of interest because a symmetry of high CN concentrations exists over both the land and the water hemisphere, unlike in the boundary layer air. Higher concentrations were also found over the extratropical frontal regime north of New Zealand.

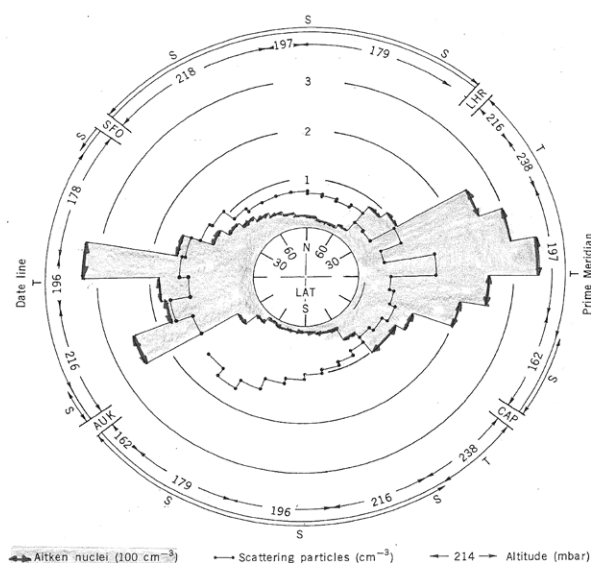


Figure 14. Global distribution of condensation nuclei at tropopause levels from the Boeing 747 SP circum-globe flight in October 1977.

Note: Data were taken from an Environment One water-based, expansion-type photoelectric condensation nuclei counter. Larger light-scattering particles are also included. Locations include San Francisco (SFO), Capetown (CAP), LHR (London), and Auckland (AUK).

Source: Hogan and Mohnen (1979).

CN concentrations in the boundary layer over land vary by orders of magnitude and over short temporal and spatial scales, depending on proximity to sources and meteorological factors, including mixing depth and clouds. This variance was demonstrated by systematic studies of CN concentrations, such as those carried out by Hogan (1966) in New York City; on the eastern shore of Lake Ontario (Oswego, New York); in a sparsely settled area within

the Adirondack State Park at Whiteface Mountain, New York; and at Yellowstone National Park in Wyoming. These sites, except New York City, were examined for a minimum amount of influence from local sources. A frequency distribution of concentration is used to describe an Aitken nuclei climate. As shown in Figure 15, the cumulative frequency distribution of CN concentrations very closely approximates a log-normal distribution at all locations, with the standard deviation and median being a characteristic of the site and season. The mean concentration levels reported by Hogan (1966) are in good agreement with the corresponding concentration levels quoted by Landsberg (1938).

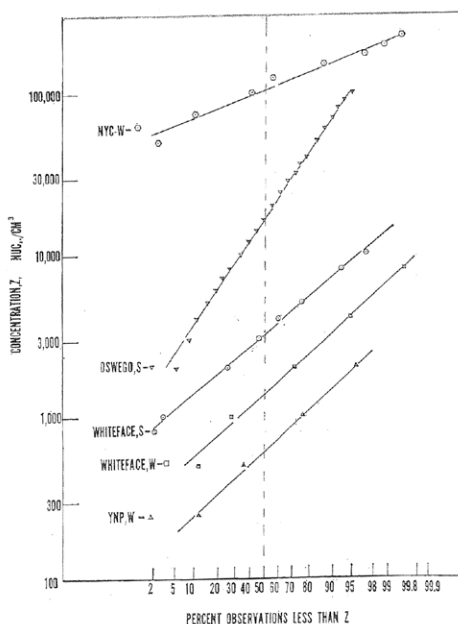


Figure 15. Representative cumulative frequency distributions of condensation nuclei concentrations at several sites in the mid-1960s.

Note: Data are from winter (W) and summer (S), covering background to highly polluted areas of the United States (New York City, Oswego, Whiteface Summit, 0.82 km altitude; Whiteface Lodge, 0.5 km altitude; Yellowstone National Park, 2.1 km altitude).

Source: Hogan (1966).

The variation of CN from the outskirts of a large settlement to its interior has been the subject of several investigations. Gemuend (1907, 1908) was the first to conduct surveys in various cities throughout Germany. In Hamburg he found in the central part of the harbor 1.4×10^5 nuclei/cm³, as against 8.0×10^4 in the court of the city hall, and 1.6×10^3 on the outskirts of town. Kiel showed a variation between 8.0×10^4 nuclei/cm³ in the center of town and 10^4 nuclei/cm³ about 2 km outside of town. In Aachen the variation was between 1.60×10^5 and 3.0×10^4 nuclei/cm³. Schmidt (1918) was one

of the first to document this dependency near Vienna (Austria). The average nuclei concentration was 1.7×10^4 nuclei/cm³ when the wind came from the open country, rose to 4.6×10^4 nuclei/cm³ when the wind had traveled 8 km from an industrial section, and became 1.9×10^5 nuclei/cm³ if the distance to the factories and dwellings downwind was within 3 km. From Innsbruck (Austria), Ginner and Hess (1937) reported as an average of many measurements 3.6×10^4 nuclei/cm³ in the center versus 1.2×10^4 nuclei/cm³ outside of town. As is now well accepted, the location of an observation place with regard to the sources of pollution is the deciding factor when analyzing CN data as to their connection with wind direction.

A perspective on the concentration differences between size fractions of the tropospheric aerosol and different measures of cloud or ice nuclei is shown in Figure 14 from 1960s observations in northeastern Colorado (Hidy et al., 1970). This location is in a rural agricultural area 100 to 200 km east of the urbanization of the region adjacent to the Front Range of the Rocky Mountains. A ground-level record in the summer of 1970 at New Raymer, Colorado, is shown in Figure 16. The data record shows an order of magnitude difference between CN and CCN concentrations (at 1.5% water vapor supersaturation) at this site and two orders of magnitude difference between optical particle counts >150 nm radius and the CCN concentrations. The concentrations of ice nuclei (IN, nominally insoluble particles assumed to be mainly soil dust) are even lower in the region. These observations for CN and CCN are consistent with the expectations from Junge's schematic picture in Figure 1.

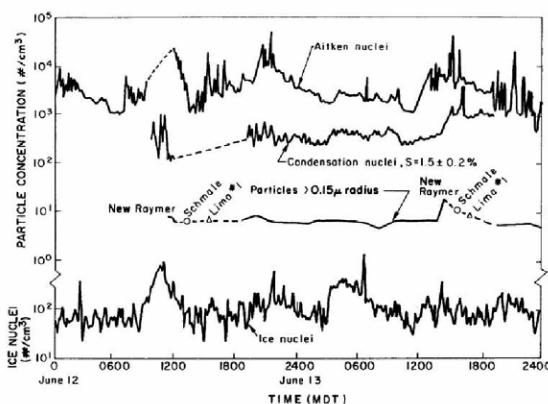


Figure 16. Observations of condensation nuclei, cloud condensation nuclei, and ice nuclei concentrations obtained in a remote area of the Great Plains in northeastern Colorado.

Note: The graph shows different characteristic measures of cloud-related particles in the lower troposphere. Each of the measures of particles involves particle size and characteristic physical properties (especially ice nuclei).

Source: Hidy et al. (1970).

Hidy and colleagues (1970) also reported typical observations for CN from aircraft flights over New Raymer in different summer cloud conditions. At 2 km above the ground, near summer cumulus cloud base, CN concentrations ranged from 4×10^3 to $>1.8 \times 10^4$ nuclei/cm³, depending on cumulus cloud presence or haze observed. Above 6.5 km altitude, the concentrations observed ranged from $>10^4$ nuclei/cm³ under clear conditions to 2×10^2 nuclei/cm³ for developed cumulus to cumulonimbus cloud conditions. Such data indicate the high degree of variability in the troposphere depending on continental air mass conditions.

Mid-continental conditions are compared with summer “background” observations in Greenland of Flyger and colleagues (1976). At the surface, CN were ~ 150 nuclei/cm³, whereas airborne observations varied from 10^2 to 10^4 nuclei/cm³. In contrast, CCN (at 0.5% water supersaturation) over the neighboring North Atlantic Ocean were ~ 12 nuclei/cm³, and IN were 0.01 to 0.1 particles/l. Both of these cloud-active nuclei levels were much lower than those in Colorado; however, the CN levels aloft over land tended to be in the upper range of those over Greenland.

One important part of Junge’s research was establishing the linkage between the CN-ion measures for particles and the atmospheric particle size distribution, as shown schematically in Figure 1. The basis for his conceptual model of the aerosol size distribution derived from his careful work with electrical mobility measurements and his observations of particle size and number from microscopic evaluations. Junge’s pioneering efforts led him to the formulation of a number-size distribution function that by and large is still valid today. Junge’s original particle number-size distribution is shown in Figure 17. The observations illustrate the abundance of Aitken (CN) nuclei in ambient air, though their contribution to total aerosol mass concentration is minor.

Scientists expanded Junge’s classical work on particle size distributions significantly in the late 1960s and beyond, once the MAAS analyzer was placed in the field. They generated a large number of particle size distributions, which ranged from remote areas to urban conditions in parts of the United States. The conditions representing photochemical smog in comparison with rural conditions in California were well described in the 1969 Pasadena experiment (Whitby et al., 1972) and later in the California Aerosol Characterization Experiment (ACHEX) (Whitby & Sverdrup, 1980). These experiments clarified the “universal” characteristics of Junge’s number-

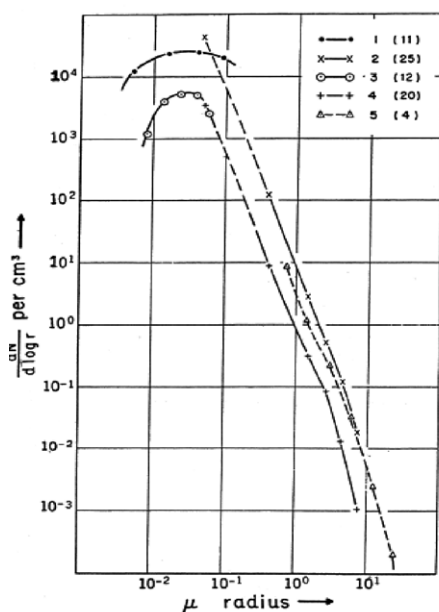


Figure 17. Jungé's average number-size distribution for tropospheric aerosols.

Note: Curves 1, 2, and 5 are measurements from Frankfurt/Main, Germany. Curve 1 represents ion counts converted to nuclei numbers. Curve 2 represents data from impactor samples. The point below $0.1 \mu\text{m}$ radius was obtained from the total condensation nuclei (CN) number under the assumption that the radius (r) interval of the CN is $\Delta \log r = 1.0$. Curve 5 represents average sedimentation data over a period of 11 days. Curves 3 and 4 are measurements at the Zugspitze, Germany, 3 km above sea level, and correspond to Curves 1 and 2 for Frankfurt. The numbers in parentheses give the number of individual measurements. The dashed curves between 8×10^{-2} and $4 \times 10^{-1} \mu\text{m}$ are interpolated to connect the ion counts or CN counts with the optical microscope determinations.

Source: Jungé (1955). Reprinted by permission of the American Meteorological Society.

size distribution and showed that the surface density-size and the volume density-size distributions were multimodal in character for tropospheric aerosols. The multimodality was not clear in the original observations reported from Jungé's (1963) assessment.

The examples provided here give a brief overview of the observations of CN and CCN related by investigators to basic tropospheric aerosol chemistry and cloud microphysics before 1975. Investigators almost universally obtained their observations of CN with Aitken-type counters, either with handheld devices or with continuous instruments, combined with the later entry of observations from electrical mobility instruments. The collection of these historical data appears to have been largely lost to the current generation of atmospheric nanoparticle investigators. Nevertheless, the data represent a rich resource of observations that characterize the presence of tiny particles in one form or another across the globe in marine and continental conditions.

As an outgrowth of interest in atmospheric nuclei, much of the post-World War II research was devoted to nuclei measurements involving cloud microphysics. The measurements of CN were embedded in the general topic of cloud microphysics and spawned sufficient interest in the atmospheric science community to organize a series of international conferences

on nucleation and condensation processes, beginning in 1955 with the participation of 40 scientists in the First International Conference on Condensation Nuclei, held at the School of Cosmic Physics at the University of Dublin. At the Second Symposium on Condensation Nuclei, B. J. Mason (1957b), London's Imperial College world authority on cloud physics of the 1950s and later head of the British Meteorology Service, commented that with the expanding knowledge of cloud microphysics, there was a move from the Aitken particle regime to focus on larger (CCN) particles as the driver for cloud formation. A reason for this shift in emphasis derived largely from the unresolved problem of accounting for growth of hydrometeors from small droplets $\leq 50 \mu\text{m}$ to precipitation size ($>1,000 \mu\text{m}$) in the time interval for cloud formation and dissipation. An analogous problem exists for nanoparticle growth to the submicrometer and micrometer size range of aerosols. Formation and growth rates across the particle-hydrometeor size spectrum remain a challenging issue for scientists today.

Some Applications for Aerosol Source Identification

An important feature of modern CN counters is their superior sensitivity, being capable of detecting ultimately a single nanoparticle with diameter larger than 5 nm by magnifying its size with condensing vapors (water or other suitable fluids) into the optically active or visible size range (around $10 \mu\text{m}$). The corresponding volume magnification of a factor 10^{10} enables a theoretical mass detection capability of less than 10^{-18} grams. Only very few instruments can match this performance level and then only with considerably more demanding technology. But even under more realistic conditions, CN counters offer applications in several different scientific, industrial, or even military areas other than atmospheric research. In general, all gas-to-particle conversion (GPC) processes are of potential interest for further investigation as to the characterization potential of a specific source or for a specific purpose (Mohnen & Lodge, 1969).

For example, it is well known that ammonia reacts with nitric acid to form ammonium nitrate particles. Ozone reacting with terpene vapor is also known to form particles. Consequently, the potential exists for detecting either of these gases in the atmosphere, provided the GPC conversion can be optimized with regard to particle detection and noninterference. Schaefer (1978) built a simple device to measure nitric acid and ozone across the United States, sampling ambient air in a plastic bag saturated with either ammonia (for

HNO_3 detection) or beta-pinene (for O_3 detection) and recording the particles formed in this reaction with a portable photoelectric CN counter of Rich (1955). Schaefer wrote, "In relatively clean air having a total concentration of particles larger than 5 nm diameter of 10^3 particles/ cm^3 , the presence of 20 parts per billion of ozone will increase the particle concentration within a couple of seconds to more than 10^6 particles/ cm^3 ." Anecdotally, in the Antarctic winter, S. Barnard apparently was able to obtain similar CN levels by squeezing an orange peel.

Ammonia and hydrochloric acid vapors react to form a visible ammonium chloride fume. In the mid-1960s, researchers from GE (Schenectady, New York) designed an instrument based on this reaction for deployment in Vietnam as a "man sniffer" (Figure 18). The idea was that people perspire and emit ammonia and thus reveal their presence in underground tunnels or in the jungle. The security-classified gas-to-particle converter used an ion molecule reaction and subsequent ion nucleation. First the air was ionized, leading to the formation of hydrated ammonium ions $\text{NH}_4^+ (\text{H}_2\text{O})_n$, and then exposed to saturated hydrochloric acid vapor (Coffey, 1972), leading to the nano-size cluster ions $\text{NH}_4\text{Cl}^+(\text{H}_2\text{O})_x(\text{HCl})_y$ that were detected in a portable, automatic photoelectric CN counter specially designed by GE for that purpose. The lowest detection limit for this device was slightly below 100 parts per trillion NH_3 in ambient air. The specially designed CN instrument without converter was used in Vietnam as a combustion sensor by dropping it from aircraft near the major supply routes through the jungle to detect and monitor vehicular traffic of the North Vietnamese army.

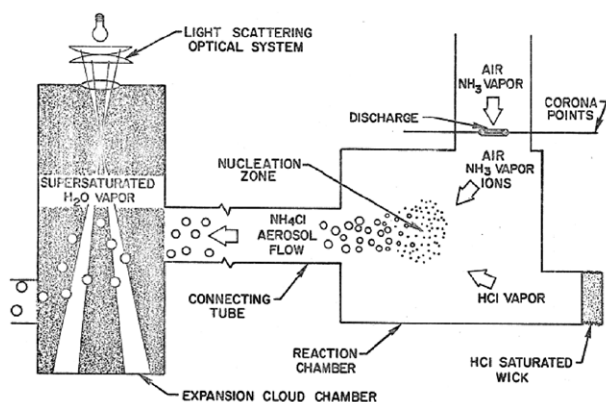


Figure 18. General Electric military photoelectric condensation nuclei counter, "man sniffer."

Note: The man sniffer measures ammonia in ambient air at concentrations >100 ppt, interpolated to connect the ion counts or CN counts with the optical microscope determinations.
Source: US Department of the Army (1971).

Combustion-produced nanoparticles from snorkeling diesel submarines were also the focus of a GE research effort, which led to the design of an airborne automatic photoelectric CN counter based on the Vonnegut (1949) design. This “submarine detector” was manufactured as Model ASR by the GE Defense Electronic Division and extensively used on aircraft during the 1950s. It is generally considered as the forerunner of the commercial GE counter introduced in 1963 (Skala, 1963).

To the extent that nanoparticles are emitted by numerous sources, including fires, heated plastic materials (macro-molecules), and electric discharges, CN counters have been put to work worldwide as process monitors or early warning detectors. Although CN detectors have not been used for routine air pollution monitoring of nanoparticles, other than for research purposes or as an indicator for highly contaminated air masses, the continuous instruments have been adopted for high-altitude flight—for example, by the US Department of Transportation (DOT) during CIAP in the 1970s (Grobeck, 1975). The measurements in the upper troposphere and lower stratosphere enabled DOT investigators to extend their knowledge of the impact of commercial and military aircraft on particle concentrations aloft. These data were also useful in assessing the importance of aircraft emissions to the inadvertent cloud nucleation at high altitude.

Toward the Present (1980–2010)

Recently, interest in nanoparticles has surged with continuing evidence of their ubiquitous presence in the atmosphere in both urban and highly remote areas. This interest has been stimulated further by evidence that their presence has environmental consequences. These minute particles also have a potential for modifying cloud processes through changes in CCN. Scientists have hypothesized that, through this microscale process, nanoparticles may be a factor in indirect forcing of climate change. Advances in instrumentation in the past 30 years for physicochemical characterization have facilitated the investigation of nanoparticle chemistry (Flagan, 1998; McMurry, 2000b). Measurements still rely heavily on the classical methods of CN counting or mobility analyzers but with greatly improved methods for size segregation and continuous, fast response counting.

Researchers around the world have developed novel experimental and theoretical methods to characterize nanoparticle formation, chemical composition, and behavior. No routine network-monitoring measurements

of nanoparticle number-size distributions, mass concentration, or chemical composition exist. However, observations have shown that these particles universally make up only a small portion of the mass concentration of particulate matter, compared with the larger particle fractions. As noted by Junge (1963) and many others, their number concentration is significantly larger than the fine and coarse fractions, and their chemical composition is distinct from these larger fractions. Recent results from North American sampling, for example, also show a difference by size fraction in the relative amounts of carbon, sulfate, nitrate, and soil dust components. Observations suggest that primary sources of tropospheric nanoparticles derive from combustion processes, especially motor vehicle emissions (Sgro et al., 2003; Zhu et al., 2004). Scientists also have documented the formation of nanoparticles in urban and rural atmospheric conditions favoring homogeneous or ion nucleation processes (e.g., Kulmala, 2004; Woo et al., 2001; Stanier et al., 2004; Watson et al., 2006). The observations suggest that these particles are composed mainly of sulfuric acid or sulfate salts and possibly some organic species.

One of the contemporary motivations for investigating nanoparticles in the atmosphere stems from concerns about environmental effects. Recently, researchers have explored the role of ultrafine or nano-aerosols in promoting adverse human respiratory and cardiovascular health effects upon inhalation (Seaton et al., 1995; Donaldson et al., 1998; Oberdörster et al., 2005; Maynard & Kuempel, 2005). A potentially important mechanism for causation of health problems by nanoparticles is pulmonary inflammation via oxidative stress (Donaldson et al., 1998). A proposed metric for determining the magnitude of the effect is total particulate surface area (Stoeger et al., 2006). Particles in the nano-range have a larger specific surface area (surface area per unit mass) than their larger counterparts, resulting in a greater dose per unit particulate mass.

On a global scale, perhaps the most important formation processes are by homogeneous, heterogeneous, ternary, or ion-induced nucleation. Once formed, nanoparticle growth after nucleation, which can be over 20 nm/hr, can occur as a result of coagulation or physicochemical uptake of low vapor pressure gases (condensation) into the particle (Weber et al., 1997). Most evidence from observations suggests that the high concentrations of nanoparticles near their origins decline rapidly as the particles coagulate or grow to form larger particles, adding to the size fraction 500 to 1,000 nm,

called the accumulation range. A few observations, however, suggest that the nanoparticles may remain stable for hours in conditions that have low concentrations of larger particles. Such growth potential links the presence of nanoparticles to a variety of phenomena, ranging from atmospheric chemical processing to modification of cloud-forming nuclei.

The global baseline conditions for CN distributions have emerged from measurements taken since the mid-1970s. Examples of the observations found in remote regions of the Southern Hemisphere are shown in Figures 19 and 20. Figure 19 displays concentrations observed by John Gras that are likely tied to natural processes. Figure 20 shows a similar long-term data record taken in Antarctica by Hogan and colleagues (1993). Here a similar seasonal cycle is observed, which almost certainly is natural in origin, perhaps linked with sulfate formation from dimethyl sulfide oxidation, the presence of sea animal or microbiota activity, or variations in tropospheric mixing.

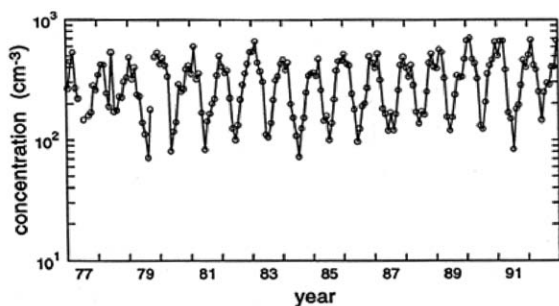


Figure 19. Long-term record of condensation nuclei observed at Aspendale, Australia.

Note: Aspendale is a relatively remote area influenced by both continental and marine air. The record indicates a seasonal condensation nuclei accumulation or production cycle in the Southern Hemisphere.
Source: Gras, personal communication (2006).

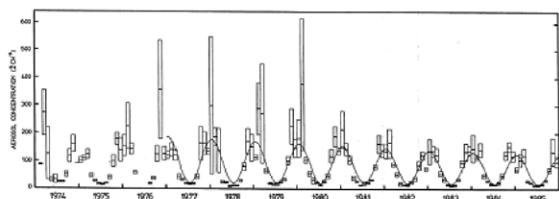


Figure 20. Long-term record of condensation nuclei concentrations observed in Antarctica.

Note: The record shows a seasonal pattern of very low concentrations with maxima in the Austral summer, presumed to be mainly natural-marine in origin.
Source: Hogan et al. (1993).

Hogan (1986) also reported latitudinal measurements from summer flights in 1977 to 1980 over the Pacific Ocean between the United States and Antarctica. He reported that, in clear air, average CN concentrations were in the range of 200 to 400 nuclei/cm³ in the upper troposphere, with maxima in the intertropical convergence zone near the equator and in the region of the subtropical jet at 25°S to 30°S. Hogan compared these findings with surface observations along a similar pathway. At the surface, minima of ~200 nuclei/cm³ appear near the South Pole and at the equator, while at ~60°S to 20°S a maximum CN was found to be ~400 nuclei/cm³. These and other results suggest the application of CN distributions as tracers of large-scale atmospheric processes.

An example of apparent post-mid-1970s trends in the ground-level CN compared with CCN concentrations in relatively remote areas can be seen in Figure 21 for the Australian data at the World Meteorological Organization (WMO) site at Cape Grim, Tasmania (Gras, personal communication, 2006). The data reported at this remote site are obtained under conditions of wind direction oriented toward clean air away from continental sources of Australia. The data are believed to be representative of clean air in the global Southern Hemisphere. Unlike the earlier marine sample in Figure 11, these data indicate a systematic increase in CN concentration, and to a lesser extent CN in winter,

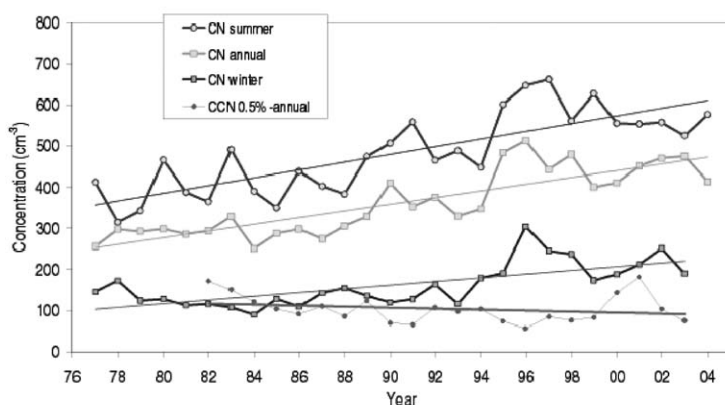


Figure 21. Trends in condensation nuclei and cloud condensation nuclei concentrations (determined at 0.5% water supersaturation) reported from a remote site in the Southern Hemisphere at Cape Grim, Tasmania.

Source: Gras, personal communication (2006).

from 1976 to 2003. In contrast the CCN tend to decrease at this location over the same period. The reason for the CN increase is unclear but presumably represents a trend in “residual” nuclei concentrations throughout the region south of Australia resulting from industrialization and perhaps large-scale vegetation fires that have occurred in Southeast Asia (Hidy, 2009).

In the 1980s, B. Bohdaine collected additional continuous, baseline CN and light-scattering coefficient data for the Northern Hemisphere. These data are available from National Oceanic and Atmospheric Administration internal reports but generally are not accessible in the reviewed literature.

Summary and Conclusions

Although the science of atmospheric nanoparticle aerosols is over a century old, and despite recent progress, much remains to be done. A considerable knowledge gap exists on quantifying the formation processes of nanoparticles as CN and how they grow to sizes that can serve as CCN and affect the earth's climate and albedo. Knowledge is also lacking on the fraction of these particles that are formed by direct emissions, nucleation of hot vapor upon cooling, or atmospheric formation of gases that undergo nucleation. Nanoparticle physical, chemical, and especially toxicological properties are incompletely understood. Many of the measurements that are needed require instrumentation that is currently under development, with special focus on elucidating the chemical composition of nanoparticles. These techniques are undergoing rapid progress, with on-line aerosol mass spectrometers now capable of characterizing the size-segregated chemical composition of particles in the >5 to 100 nm diameter range.

The characterization of nanoparticles in the atmosphere has generated increased interest in recent times because of new instrumentation for the measurement of their physical and chemical properties. Although this interest has stimulated the generation of a substantial body of new information about atmospheric particles, a large body of historical knowledge also is accessible dating back to the 19th century. Indeed some of the earliest truly scientific interests in atmospheric aerosols derived from observations of the total number of particles in the air, dominated by the nanoparticle range. The observations of Aitken and his many successors, including C. Junge, H. Landsberg, and later A. Hogan, should not be neglected by contemporary scientists in their quest for understanding of the broad and diverse range of aerosols present in the earth's atmosphere.

Today, with air pollution as a continuing concern and with new instrumentation and methods, the pendulum appears to have swung back to the nano-range for another generation of researchers (Weber et al., 1997; Kulmala, 2004; McMurry et al., 2005).

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