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The History of Condensation Nucleus Counters

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ABSTRACT. Condensation of supersaturated vapors has been used for more than a century to grow small aerosol particles to sizes that can be detected optically. This paper discusses the history of instruments that use condensation to detect particles. I divide this history into two main sections. The first of these focuses on the development of expansion-type instruments including the "dust counters" in which John Aitken played the decisive role and "photoelectric nucleus counters" primarily by L. W. Pollak and coworkers. The second section deals with the development of steady-flow condensation nucleus counters (CNCs) in which Jean Bricard and coworkers played the decisive role. The importance of calibration methodologies is also pointed out. Refinements by instrumentation manufacturers and many aerosol scientists have led to the reliable, accurate instruments that are widely used today.

INTRODUCTION

Ultrafine particles (particle diameter $<0.1\ \mu$m) can be detected by electrostatic methods and by condensational growth to sizes that are large enough to be detected optically.[1] Electrostatic methods can only be used with charged particles. The most commonly used electrostatic technique involves measuring the current delivered to a Faraday cup by a stream of charged particles (e.g., Liu and Pui 1974). More recently a number of single-particle electrostatic detection schemes have been developed primarily by the mass spectrometry community for the study of macromolecules. These include conversion dynodes and microchannel plates (Zimmermann et al. 1994) and charge-sensitive devices that permit the detection of individual charged particles (Fuerstenau and Benner 1995). Electrostatic techniques often can be used in conjunction with electrostatic size classification schemes including electrical mobility classification (Knutson and Whitby 1975), time-of-flight mass spectrometry (Zimmermann et al. 1994), or particle beam mass spectrometry (Roth and Hospital 1994; Ziemann et al. 1995). The primary limitation of electrostatic detection is sensitivity. In many practical applications ultrafine particles do not carry enough charge to be detected using single particle electrostatic detectors, and

[1] Rayleigh scattering can also be used to detect populations of ultrafine particles. This is an important methodology for systems with high concentrations, but usually cannot be used to detect individual ultrafine particles because of the sixth power dependence of light scattering intensity on particle size for particles small compared to the wavelength of scattered light.

Faraday cup detectors typically require much higher concentrations than can be detected using single-particle-counting condensation nucleus counters (CNCs). The history of electrical aerosol detectors is discussed by Flagan (1998).

Condensation is the only technique available for detecting neutral gas-borne particles that are too small for optical methods. Commercially available instruments can detect particles as small as 3 nm, and because particles can be counted individually, the minimum concentration that can be detected is limited only by instrument noise (which can be made negligibly small) and by counting time. The ability of CNCs to cover a wide range of sizes and concentrations has made them the most commonly used ultrafine particle detector currently in use. One curious feature of condensational detection schemes is that minute quantities of material can be detected with excellent signal to noise. For example, the mass of a 3 nm particle is $\sim 10^{-20}$ g. A corollary to this is that the original particle typically constitutes only a minuscule portion (as small as 1 part in 10^{11}) of the detected droplet, since particles are grown to $\sim 10\ \mu$m before they are counted.

Several other papers provide important historical perspectives on CNCs. *The Collected Scientific Papers of John Aitken*, published shortly after Aitken's death (Aitken 1923), provides fascinating lessons in science from a bygone era. This collection includes Aitken's work on the design and use of "dust counters" and illustrates his incisive approach to experimental research. These papers contain many remarkable insights and make delightful reading. Landsberg published a comprehensive treatise of atmospheric condensation nuclei (Landsberg 1938), including a critical evaluation of measurement methodologies. Pollak's and Nolan's papers (Pollak 1959; Nolan 1972) focus primarily on their respective contributions to the development of CNCs. Miller and Bodhaine (1982) provide a critical historical review of expansion ratios and implications for the instrument performance, and Wagner (1982) reviews previous work on condensation. Podzimek and Carstens (1985) review the history of Aitken nuclei counters, with an emphasis on phenomena that affect the performance of these instruments, such as expansion method and expansion ratios, particle growth rates, material-dependent response, etc. Podzimek and Carstens (1985) and Jaenicke (1988) provide summary tables of historically important condensation nucleus counters and their operating characteristics. Numerous authors (e.g., Jaenicke and Kanter 1976; Hogan 1979; Podzimek et al. 1982; Wilson et al. 1983) provide brief but illuminating historical backgrounds to their work.

A few words on terminology are needed. Various authors have adopted different standardized terminologies. For example, Podzimek and Carstens (1985) define "Aitken Nuclei Counters" as expansion instruments that operate with water supersaturations of 200% to 350% and "condensation nuclei counters" as instruments that operate in an indirect counting mode with a vapor other than water. Nevertheless, the terminology used to describe such instrumentation continues to evolve, and no standard has been adopted by the community. Condensation Particle Counter (CPC) has recently begun to emerge as more accurate and less ambiguous than CNC. Nevertheless, many authors continue to use "condensation nuclei counter" or "CNC" to generically describe instruments that rely on condensation to detect particles, regardless of the working fluid, method of producing the supersaturated vapor, etc. When discussing individual instruments, I use the terminology of the original author.

In this paper I have not attempted to refer to or discuss everything that has been published on CNCs. I have found hundreds of papers on the subject and am certain that I have not found them all. Instead, I have focused primarily on work that, in my opinion, has had a lasting impact on CNC design. This includes a more extended discussion of steady flow instruments, which are so important today, than has previously been published. I know that I have not done justice to the entire field. Much of the literature is not readily available and/or is published only in languages

with which I am unfamiliar. In particular, the Russians have done much original work with CNCs, and I have not had access to most of this work. It is my hope that other authors will fill in critical gaps that I have missed. I have included some developments that struck me as particularly interesting even though they may have played only a minor role in the history of CNCs.

This paper is divided into two major sections. The first of these deals with expansion-type instruments of both the manual-counting and photoelectric types. The second section deals with continuous flow CNCs, of which three major types have been reported. I've also included a discussion on CNC calibration, which played an essential role in establishing quantitative relationships between concentration and instrument output.

EXPANSION-TYPE INSTRUMENTS

Instruments that Required Qualitative Assessment of Fog Formation or Counting of Droplets

The formation of "clouds" upon the expansion of air containing water vapor was discussed by Espy (1841). He built the "nephelescope" shown in Figure 1, which included a pump used to draw aerosol into the container labeled "b" and to pressurize the aerosol to a known value above atmospheric. Adiabatic expansion was then achieved by opening the stopcock. He found that if the air in the chamber contained enough water vapor, and if the degree of expansion was sufficient, then cloud formation occurred. Based on laboratory measurements with his nephelescope he concluded the following:

> "When the air near the surface of the earth becomes more heated or more highly charged with aqueous vapor, which is only five-eighths of the specific gravity of atmospheric air, its equilibrium is unstable, and up-moving columns or streams will be formed. As these columns rise, their upper parts will come under less pressure, and the air will therefore expand; as it expands it will grow colder about one degree and a quarter for every hundred yards of its ascent, as is demonstrated by experiments on the nephelescope."

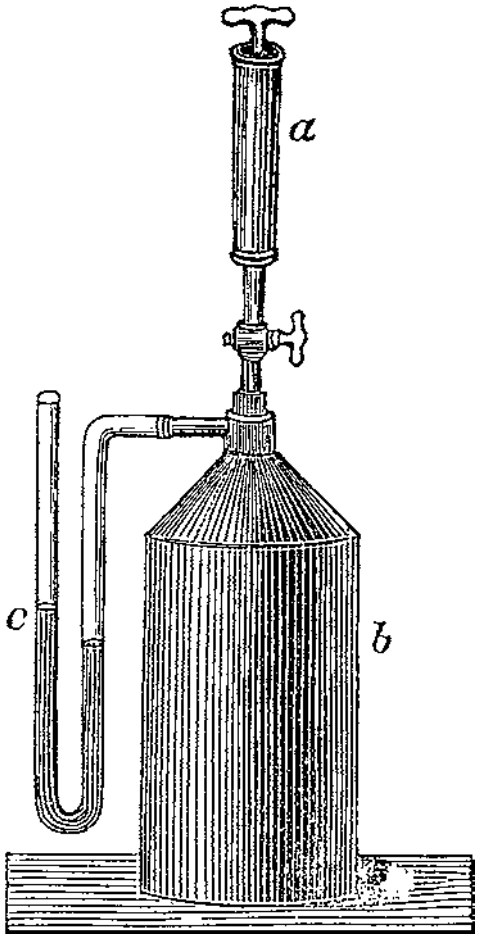

FIGURE 1. Nephelescope used to study the formation of clouds by expansion of moist air (Espy 1841).

Espy was not aware that, in the atmosphere, condensation occurs on particles. Based on his work he was enthusiastic about the possibility of producing artificial rain by the judicious use of fires.

Coulier (1875) was apparently the first to publish work showing that when air is expanded adiabatically condensation occurs more readily in unfiltered air than in filtered air. This discovery that particles serve as "condensation nuclei" is

the basis for particle detection by condensation nucleus counters. Coulier's apparatus consisted of a transparent flask with a rubber bulb for reducing the pressure in the flask. The extent of condensation was qualitatively determined by the cloudiness within the chamber.

John Aitken's research on condensation began in 1875 and continued for more than 40 years. Ill health prevented him from pursuing a career in engineering, for which he was trained. His investigations into condensation were initiated in response to his interest in the broad topic of phase transformations (Aitken 1880). He was aware that if suitable care is taken water can be cooled below its freezing point and reasoned that water vapor could similarly be cooled below its condensation point if the free surfaces provided by "dust" particles were removed. He used a cotton-wool filter to remove particles from an air stream and showed that under certain conditions "air that was free from dust gave no cloudy condensation when mixed with steam, and that the supersaturated air remained perfectly clear." When the particles were not removed, condensation was observed. In this early work he observed that "there seems a possibility of there being some relation between dust and certain questions of climate, rainfall, etc." and that "combustion under all conditions is bad as a fog-producer" and recommends that means be made to measure the composition and concentration of atmospheric dust. Although Coulier's work was published five years before this paper, Aitken was not aware of it until Groneman brought it to his attention (Groneman 1881).

To provide more quantitative information, Aitken developed the "dust counter" shown in Figure 2 (Aitken 1888). Measurements consisted of first filling flask A with filtered air. Using pump B this air was adiabatically expanded to remove by condensation any particles that may have penetrated through the cotton wool filter. A small quantity of aerosol ($\sim 1\ cm^3$) was then drawn into flask A from flask G; the burette N was used to measure the amount of aerosol delivered to flask A. Pump B was then activated to produce a known expansion. Condensed particles that settled onto stage O were counted with the magnifying glass S. Stage O was illuminated with light from a gas flame R that was focused using the spherical flask filled with water Q. The aerosol concentration was assumed equal to the number of particles on the stage divided by the gas volume vertically above the stage. This instrument underwent several refinements described in his paper of the following year (Aitken 1888–1889).

Although Aitken had no difficulty obtaining reproducible measurements with his dust counter, other investigators expressed an interest in an instrument that was simpler to use and more reliable. This led to the development of the Aitken "Pocket Dust-Counter" shown in Figure 3 (Aitken 1890–1891). This elegantly designed instrument "is so constructed, that when the different parts are unscrewed they fit into a case 4 3/8 inches by 2 1/2 inches by 1 1/4 inches deep, or little larger than a well-fitted cigar case." It came complete with an integral pump P, a mirror for focusing light onto the collection stage R, and a magnifying glass M for counting collected particles on stage R. The pump barrel was graduated to permit the introduction of a known volume of air, as shown in G, and for providing reproducible expansions. The Aitken Pocket Counter was used widely for more than 50 years.

Aitken's work is as remarkable for its scientific contributions as for its contributions to instrument design. I am particularly impressed with his astute observations regarding photochemically-generated pollution aerosols. He conducted atmospheric measurements that showed aerosol concentrations were higher when the wind was blowing from industrial sources and that the impact of these pollution sources was exacerbated by sunlight, high relative humidities, and low wind speeds. He also conducted controlled laboratory experiments to confirm the hypotheses he formed through his atmospheric observations. This laboratory work included the demonstration that sulfurous gases emitted by coal combustion contribute to air pollution. Based on this work he concluded the following (Aitken 1911):

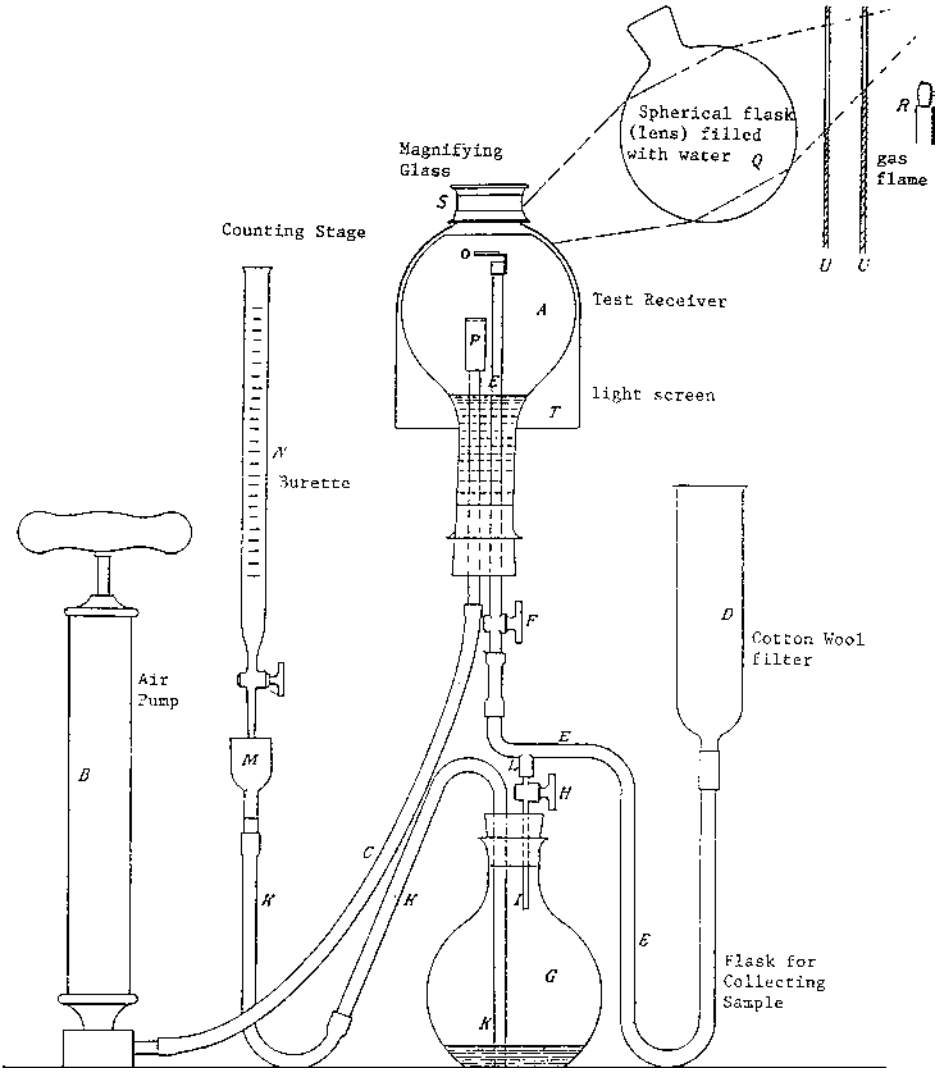

FIGURE 2. John Aitken's Dust Counter for measuring particle concentrations. Reproduced by permission of the Royal Society of Edinburgh from *Transactions of the Royal Society of Edinburgh*, volume XXXV (1887–1890), pp. 1–20.

"Though this investigation clearly shows that the sun produces certain kinds of fogs, yet it is by no means here contended that it is to be censured for their appearance. It would rather appear that it is doing its best to show us the state of pollution into which our modern civilization has brought our atmosphere, as it only inflicts these fogs on the areas upon which man has thrown the waste products of his industries and converted the atmosphere into a vast sewer, as a penalty for something wrong in his methods."

C. T. R. Wilson developed a refined expansion cloud chamber that he initially used to study homogeneous nucleation. His early work involved precise measurements of expansion ratios that led to cloud formation in the presence of dust-free air saturated with water vapor (Wilson

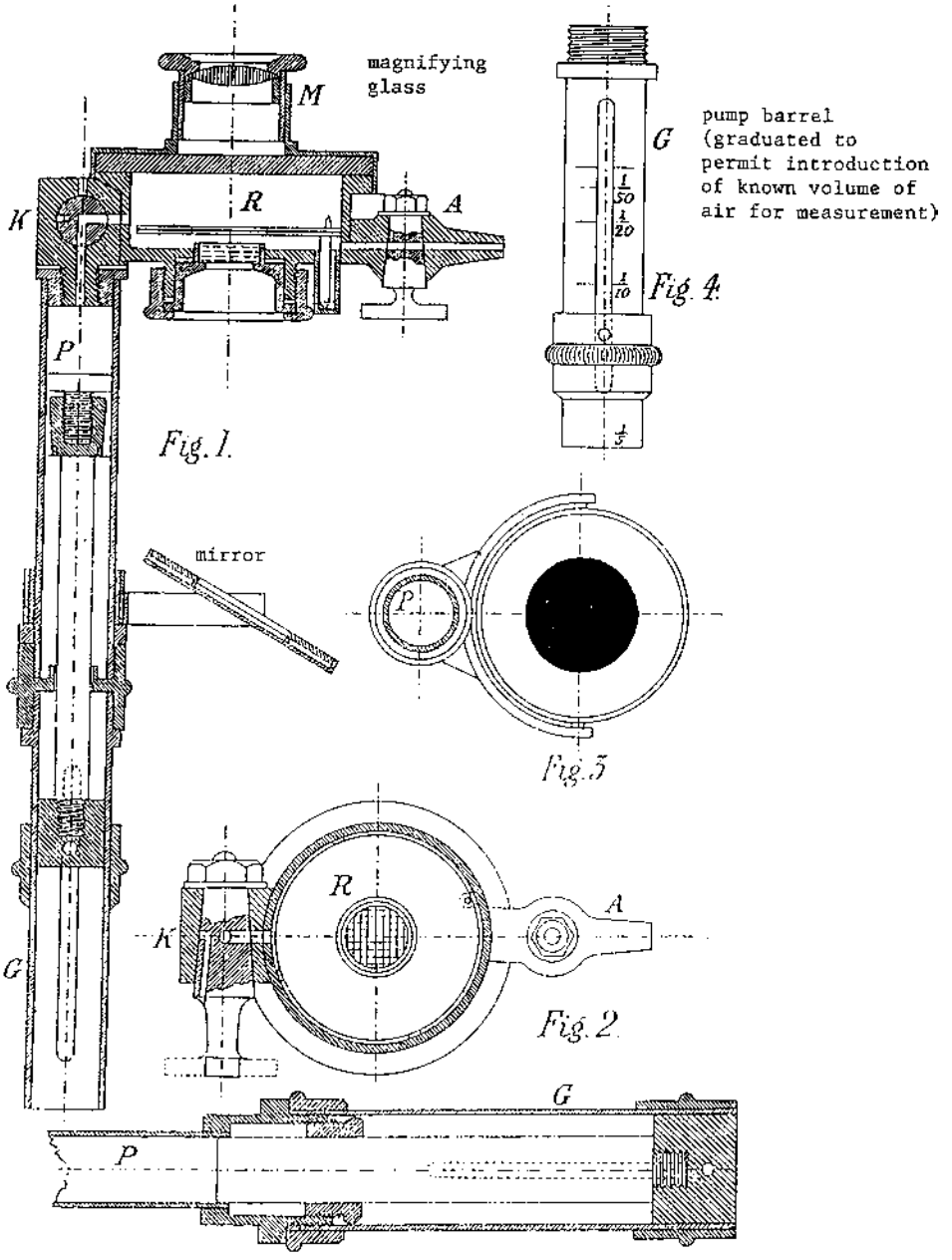

FIGURE 3. John Aitken's Pocket Dust Counter. Reproduced by permission of the Royal Society of Edinburgh from *Proceedings of the Royal Society of Edinburgh*, volume XXVIII (1890–1891), pp. 39–52.

1897). He found that after particles are removed, cloud formation will not occur until the volume expansion ratio equals 1.252. He also found that for volume expansion ratios between 1.41 and 1.42 a dense fog that was blue or blue-green in color appeared; this fog became white when expansion ratios exceeded 1.44. Shortly thereafter he showed that condensation occurs on negative

ions at expansion ratios of 1.25–1.28 and on positive ions at expansion ratios of 1.31 (Wilson 1899). The fogs that were observed above 1.4 were due to homogeneous nucleation. This work led to his invention of the Wilson cloud chamber (Wilson 1912), which played a decisive role in elementary particle research and for which he was awarded the Nobel Prize in physics in 1929. Wilson's major contribution to CNC design was the determination of precise expansion ratios that should be used to avoid ion-induced and homogeneous nucleation. His work on homogeneous nucleation was also of fundamental importance to aerosol science. As was the case with Aitken, Wilson built his own instruments and usually worked independently without the assistance of colleagues or students. Although his instruments were often simple, he worked hard at perfecting their designs so that they provided highly accurate and reproducible results. Biographers mention that both Aitken and Wilson avoided the distractions of administrative work in professional societies or academia that would have diminished the impact of their scientific careers.

Scholz developed a large (Scholz 1931) and a small (Scholz 1932) particle counter ("Kernzählers") that improved on Aitken's design. As with the Aitken instrument, Scholz's counters included a built in pump for expansion and required manual counting of droplets that deposited on a collection stage. The small counter was a "pocket" counter that could easily be transported. The large counter was equipped with a cylindrical condenser that permitted one to distinguish between charged and neutral particles and that also operated with variable expansion ratios. Scholz's designs reduced the amount of leakage that occurred during expansion in instruments of Aitken's design. Scholz found that his large and small counters agreed with measurements from a pair of Aitken pocket counters to within experimental error, but that the deviation of a set of measurements obtained with his large counter is far less than with the Aitken counters. Blanchard (1992) reported that when he worked in the laboratory of Alfred Woodcock at Woods Hole in the early 1950s he used both an Aitken and Scholz counter. He found the Scholz counter easier to use, and he worked with it for 15 years. This Scholz counter was obtained from Landsberg, who brought it from Germany in 1934.

Junge (1935) developed an expansion counter that replaced the microscope and collection stage of earlier instruments with a camera that photographed the number of suspended droplets in a known volume. Another significant innovation of this instrument was its use of variable expansion ratios with a given aerosol sample. Junge reasoned that size distributions could be determined if concentrations of a given aerosol were measured over a range of saturation ratios. This is the first use of "Kelvin-effect sizing" of which I am aware. Junge (1961) later adapted this photographic recording technique in a balloon-borne Aitken nuclei counter for the first quantitative measurements of aerosol vertical distributions in the stratosphere up to ~30 km altitude. In order to avoid the pressure-dependent response that occurs with instruments of this type, they injected filtered air prior to expansion so as to raise the pressure by one half atmosphere above ambient. These measurements of Aitken Nuclei, along with measurements of "large" (>0.3 μm) particles collected with an impactor, led to the discovery of the "Junge aerosol layer" (Junge et al. 1961), which they concluded was formed in the stratosphere by chemical transformations of sulfur-containing gases.

The Kanter Photographic Condensation Nuclei Counter (KPCNC) of Jaenicke and Kanter evolved from the instruments of Scholz and Junge (Jaenicke and Kanter 1976). In this automated instrument the aerosol was compressed to a pressure 1.21 times atmospheric. Saturation was achieved by permitting sufficient time for water to diffuse from the wetted walls of the expansion chamber into the aerosol. Repeatable expansion rates were achieved by expanding air in the chamber to the atmosphere through an expansion valve. The aerosol concentration was determined by using a camera to

photographically record the number of droplets in a known volume of air.

Kassner et al. (1968) developed the fully automatic University of Missouri at Rolla-Absolute Aitken Nuclei Counter (UMR-AANC). This instrument utilized a large (15,000 cm^3) expansion chamber to minimize errors associated with heat transfer and particle diffusion to the walls and made use of photographic recording to determine the number of activated droplets. Aerosols were diluted to a level that avoided counting errors or vapor depletion that can occur at high concentrations. This instrument was used to evaluate the calibrations of relative instruments including the GE, Environment-One Rich-100, Gardner and Pollak instruments (Saxena et al. 1972). They found that the UMR-AANC was systematically higher than all of the other instruments, suggesting that their responses were based on calibrations that underestimated the true Aitken Nuclei concentration.

Photoelectric Expansion Type Instruments

Bradbury and Meuron (1938) developed the first fully automatic expansion-type CNC shown in Figure 4. The instrument, which they refer to as a "Wilson Cloud Chamber," was driven by the drive shaft connected to pulley G. The function of this instrument is described in the original publication as follows:

> "Immediately following an expansion, the cams C lift the valves and air passes through the chamber flowing in from outside. This flushing continues slowly until approximately four minutes before the next expansion at which time the valves close and the air comes to equilibrium inside the chamber. Meanwhile a commutator, also attached to the shaft driving R, has closed the circuits for the light through L and the recording of light by the galvanometer. The expansion then takes place, and the deflection of the galvanometer is recorded. This process is then repeated continuously."

They calibrated their instrument using an Aitken Pocket Counter.

At about the same time that Bradbury and Meuron were conducting their research at Stanford University, Pollak and colleagues began the development of photoelectric instruments in Prague (Pollak and Fuchs 1936, 1937, 1938). Pollak moved to Dublin late in the decade and, with W. A. Morgan, developed a photoelectric nucleus counter early in 1940 (Pollak 1959). Pollak and colleagues continued to work on photoelectric nucleus counters through the 1950s, publishing a long series of papers that described many refinements on instrument design and calibration. Their work also included refinements on the design on manual counting instruments. I focus here on the "Model 1957 photoelectric nucleus counter" that was used for many years as a secondary calibration standard for other photoelectric instruments and is still in use today.

The Model 1957 Pollak counter is shown schematically in Figure 5 (Metnieks and Pollak 1959). This instrument consists of a 58.74 cm cylinder that is lined with a 2.5 cm i.d. porous ceramic liner. The light source and photoelectric selenium cell are isolated from the cylindrical expansion chamber by electrically heated glass plates. A manual pump is used to bring the pressure in the instrument to 1.21 above atmospheric after which 45 s is provided to allow the aerosol to become saturated by diffusion of water vapor from the wetted ceramic liner. The aerosol is then expanded through a stopcock to atmospheric pressure. The attenuation through the cloud produced by condensation is measured with a photoelectric cell. The Model 1957 was the culmination of Pollak's work and has been used since the mid 1970s for regular daily measurements at Barrow, AK, the South Pole, Mauna Loa, HI, and Samoa. It is also used as a historical reference method by CSIRO in Australia.

Automated photoelectric condensation nuclei counters were developed at General Electric's Research Laboratory beginning in the 1950s. Volker Mohnen and George Skala provided the following brief summary of this work in their letters to me. Dr. Bernard Vonnegut was issued U.S. patent No. 2,684,008 in 1954 for a

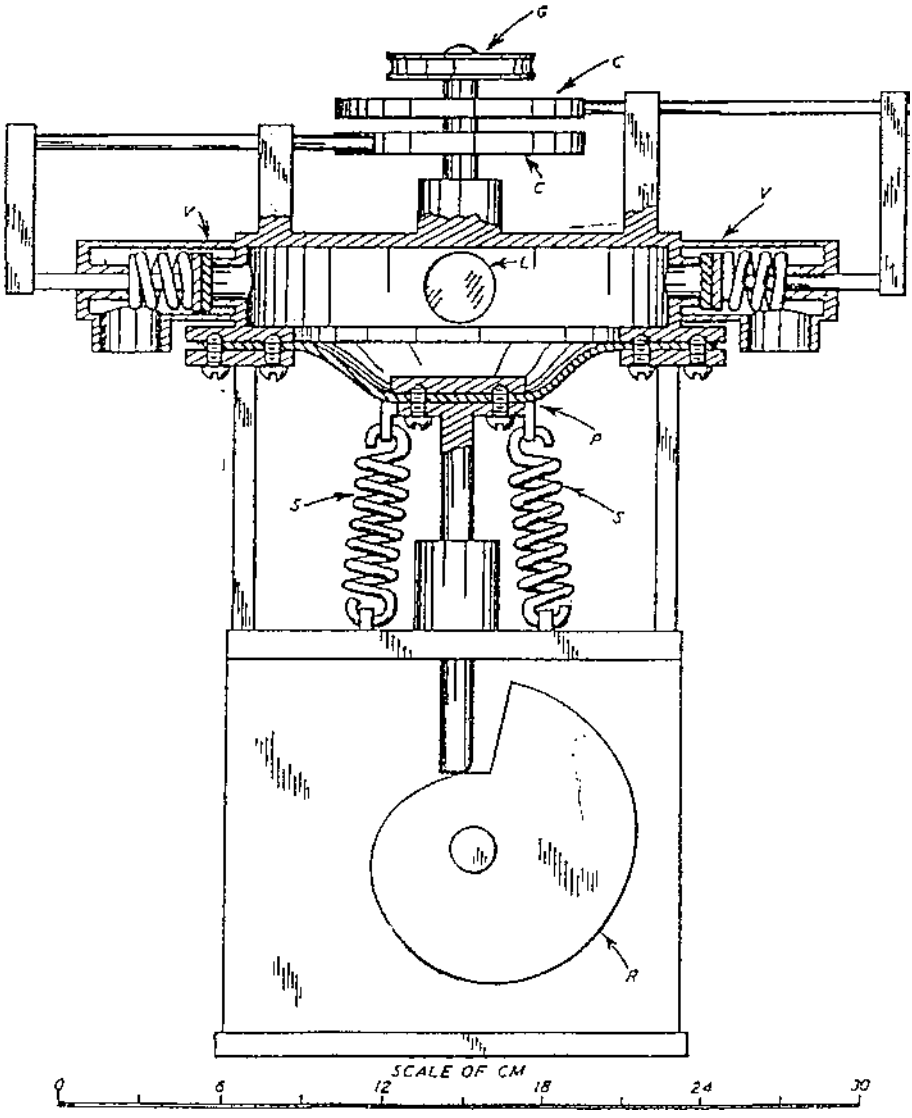

FIGURE 4. The first fully automatic expansion-type CNC. (N. E. Bradbury and H. J. Meuron, *Terr. Magn.*, volume 43:231–240, 1938, copyright by the American Geophysical Union.)

condensation nuclei detector capable of producing a continuous output of nuclei concentration. Vonnegut (1949) first described an instrument of this type. Mr. Theodore Rich then directed work leading to the development of the ASR series of instruments that were manufactured by the General Electric Defense Electronics Division. These instruments were used on aircraft during the 1950s to search out snorkeling diesel submarines. The General Electric team also developed the "people sniffer" that was used during the Vietnam war. It was a battery-operated detector that could be carried in a backpack or in a helicopter. It converted ammonia to ammonium chloride particles that were detected using the built in CNC. Most of the details of this work

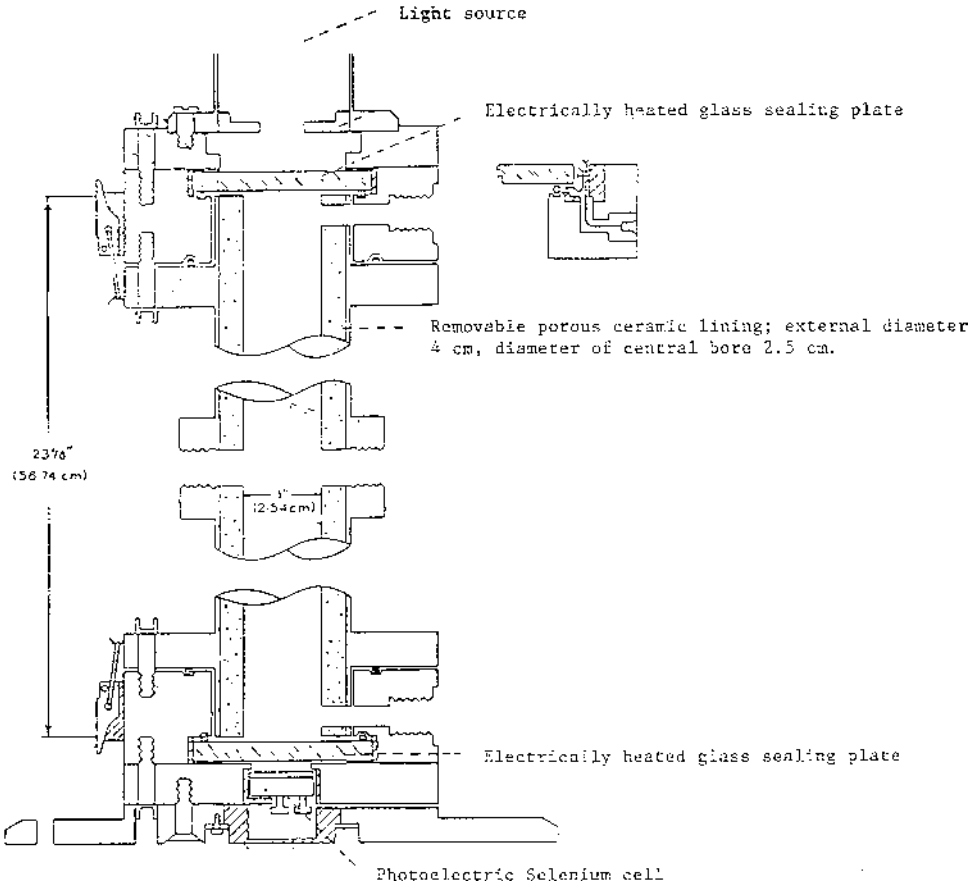

FIGURE 5. Model 1957 Pollak counter (Metnieks and Pollak 1959).

were classified and have not been openly published. It is likely that additional information could be made available through the Freedom of Information Act.

A number of commercial instruments were developed by the team that had been associated with the General Electric Research Laboratories starting in the mid 1950s. Rich (1955) developed the portable photoelectric counter that was marketed by Gardner Associates. This instrument provided an initial rapid expansion followed by a further expansion at a slower rate that was intended to permit distinction between ultrafine aerosols and larger particles. General Electric marketed several commercial models of their automatic CNCs; the first of these "continuous condensation nuclei counters" was described by Skala (1963). When Ted Rich and George Skala and others left General Electric to form Environment/One, a new series of continuous flow photoelectric instruments was developed. The first of these was the Rich 100, which came on the market in 1973. An updated version of this instrument, the Rich 200, is still on the market. The CIRRUS fire detector, which draws air from a variety of locations into a cloud chamber, is currently produced by of Environment/One.

The University of Vienna group developed the Size Analyzing Nuclei Counter (SANC) to study condensational growth (e.g., Wagner

1982; Szymanski and Wagner 1983). This instrument uses a fast (5 ms) adiabatic expansion of a 130 cm^3 volume to produce the supersaturated vapor; droplet growth during the subsequent 100 ms is measured using a laser to illuminate an 8–30 mm^3 scattering volume in the center of the expansion volume. Time-dependent droplet sizes are inferred using Mie theory from measurements of scattering intensity at a known scattering angle. Absolute concentrations are determined from simultaneous measurements of light transmitted through the monodisperse aerosol cloud (Liu et al. 1982; Szymanski and Wagner 1990). This instrument is unique among expansion-type instruments in that it provides absolute measurements of concentration without resorting to empirical calibrations or single-particle counting. More recently Szymanski (1992) developed an approach involving Monte Carlo simulation for measuring particle concentration in highly concentrated systems that are affected by multiple scattering. The SANC was also used to measure the water vapor supersaturation required to initiate condensational growth on monodisperse NaCl and DOP aerosols in the 13 to 100 nm diameter range. They found that the supersaturation required for DOP was in good agreement with predictions of the Kelvin Equation, but that the Kelvin equivalent size for NaCl was about a factor of 4 higher than the electrical mobility diameter, presumably due to the solubility of NaCl in water (Liu et al. 1984).

STEADY-FLOW CONDENSATION NUCLEUS COUNTERS

Three types of steady-flow CNCs, differing in the approach used to produce the saturated vapor, have been described. These include laminar flow CNCs that utilize forced convection heat transfer to obtain a supersaturated working fluid, mixing-type CNCs, and segmented thermal diffusion instruments. Mixing-type instruments include those that mix warm and cool streams containing the condensable vapor to achieve supersaturation and those that achieve supersaturation by mixing two vapors that undergo multicomponent condensation.

Laminar Flow Forced Convection Heat Transfer CNCs

Rosen et al. (1974) developed the steady flow thermal gradient diffusion cloud chamber (TGDCC) to obtain better measurements of aerosol concentrations in the stratosphere. A schematic of their instrument is shown in Figure 6. The aerosol was first diluted by passing a portion of the flow through a filter to bring concentrations down to a level that could be accurately counted by the photoelectric particle counter. The aerosol then flowed through an annular space in which the outer walls were maintained at low temperature with an ice bath. The temperature-controlled center rod was maintained at an elevated temperature and was kept moist with the working fluid; data were presented with water as the working fluid. The temperature gradient across the annular gap led to supersaturation of the water vapor and subsequent condensational growth of particles prior to their detection by the optical particle counter.

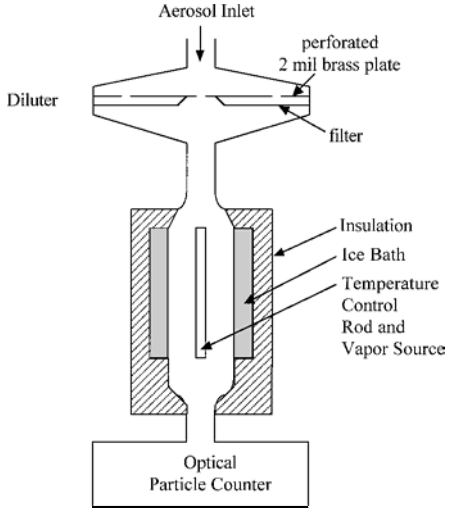

FIGURE 6. Steady-flow thermal gradient diffusion cloud chamber for stratospheric aerosol measurements (Rosen et al. 1974).

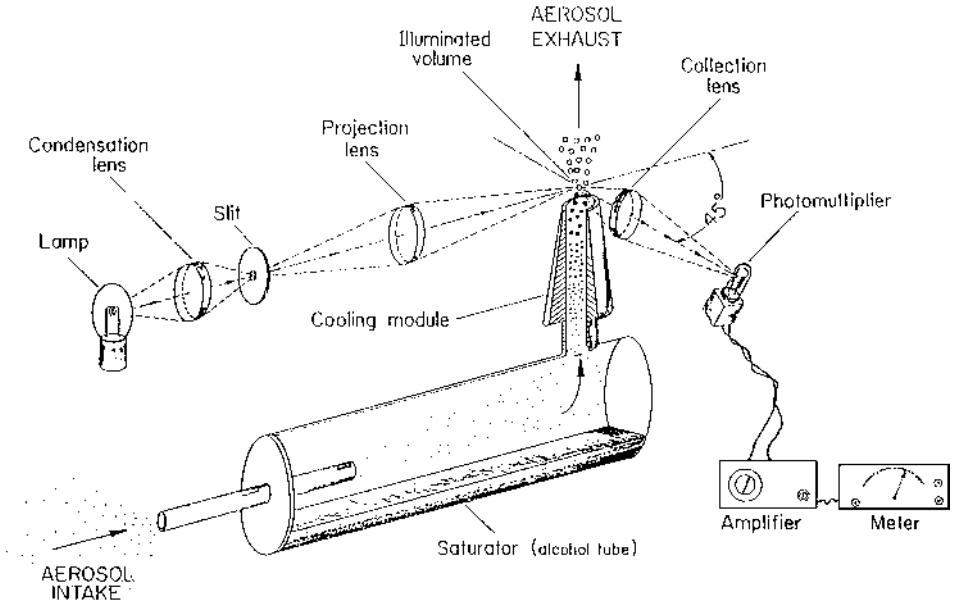

FIGURE 7. Continuous flux condensation nuclei counter. (Republished with permission of Academic Press from "Detection of ultra-fine particles by means of a continuous flux condensation nuclei counter" by J. Bricard, P. Delattre, G. Madelaine, and M. Pourprix in *Fine Particles: Aerosol Generation, Measurement, Sampling, and Analysis*, edited by B. Y. H. Liu, 1976, conveyed through Copyright Clearance Center, Inc.).

Airflow through the annular gap involved "some degree of turbulence."

Bricard et al. (1976) played an important role in developing modern steady-flow condensation nucleus counters of this type. A schematic diagram of an early instrument reported by this group is shown in Figure 7. After the aerosol is saturated with the working fluid (ethanol or butanol in this case) it flows through a Peltier (thermoelectric) cooler where the supersaturation is achieved. At the exit from the condenser, droplets flow through the sensing volume of the optical detector where they are counted individually. Unlike most modern instruments, this instrument did not necessarily count all particles leaving the condenser. Instead, the sensing volume could be adjusted to an optimal size, depending on aerosol concentrations. Large sensing volumes were used for low concentrations to reduce counting times, and small sensing volumes were used for high concentration to reduce coincidence (i.e., more than one particle simultaneously in the sensing volume).

The French group studied the response of their instrument to condenser temperature and pressure and also investigated the performance of various working fluids. They showed that ion-induced nucleation occurs when the temperature difference between the condenser and saturator exceeds a given value and that homogeneous nucleation occurs at a slightly greater temperature difference. Aerosol measurements are done at temperature differences that are somewhat below these values. They also found that counting efficiencies decreased with decreasing pressure due to the decrease in the signal from the photomultiplier tube detector and approached zero at pressures of $\sim$60 mm Hg, corresponding to a pressure altitude of $\sim$17 km.

Bricard and coworkers understood that the optimal working fluid for an instrument of this type required a vapor pressure at typical ambient temperature (25–30°C) that was large enough to grow particles in the condenser to a size that can easily be detected optically (0.5–15 μm), yet not so large that particles would be lost by

sedimentation or impaction. They also understood the critical role of vapor diffusivity, which determines the rate of vapor depletion to the condenser walls. It is desirable to choose a working fluid having a small diffusivity in air, thereby ensuring that particles are exposed to elevated supersaturation as long as possible during flow through the condenser. A more quantitative theoretical understanding of the performance of these instruments evolved through the analyses of Holländer (1980) and Metayer et al. (1982). These analyses, ultimately, rely on the theory of forced convection heat and mass transfer (Graetz 1885) to calculate radial and axial vapor supersaturation profiles in the CNC condenser. More recently, the use of numerical computations to model the performance of instruments of this type has been reported (Ahn and Liu 1990a, 1990b).

Another forced-convection heat transfer "continuous flow condensation nucleus counter" was developed independently at about the same time by David Sinclair and coworkers (Sinclair and Hoopes 1975). They saturated the aerosol with ethanol before it flowed into a cylindrical tube that was cooled either with thermoelectric devices or by mechanical refrigeration. The aerosol concentration was determined by measuring the percent light transmittance along the axis of the cylindrical condenser, much as was done with Pollak's photoelectric nucleus counters. Thus, this instrument was not capable of counting individual particles and had a concentration range of $500–10^6$ cm^{-3}. Sinclair and Hoopes reported that the aerosol fogs were limited to an annular region close to the walls of the condenser during laminar flow operation. They therefore inserted orifices in the saturator and condenser to induce turbulence. This led to a more uniform aerosol cloud in the condenser.

The first commercially-produced forced convection heat transfer CNC was the TSI 3020 (Agarwal and Sem 1980). A schematic of this instrument is shown in Figure 8. This instrument

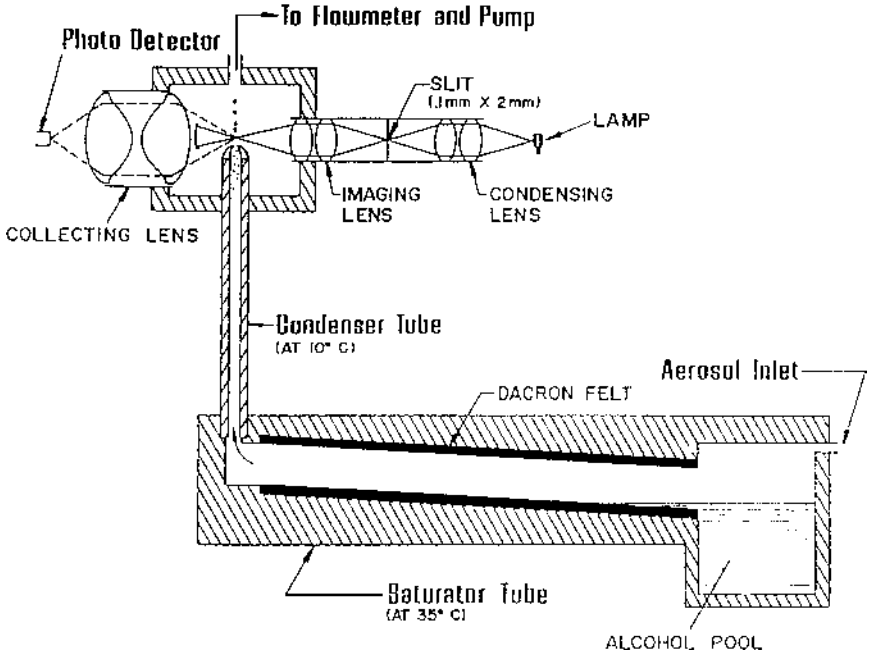

FIGURE 8. The TSI 3020 continuous flow, single-particle counting condensation nucleus counter. Reprinted from the *Journal of Aerosol Science*, volume 11, J. K. Agarwal and G. J. Sem, "Continuous flow, single-particle-counting condensation nucleus counter," pp. 343–357, Copyright (1980), with permission from Elsevier Science.

operates in the single-particle counting mode for concentrations below ~1000 cm^{-3} and in the "photometric" mode for concentrations higher than this. The single particle counting mode involves the detection of forward-scattered white light from a halogen lamp. The photometric mode involves measurement of the d.c. level of light scattered by the aerosol cloud at the exit of the condenser. While the single-particle count mode provides an absolute measurement of concentration, the photometric mode requires an empirical calibration. Butanol was selected as the working fluid because it was found to absorb water more slowly than isopropanol, which was used initially. Absorbed water leads to a decrease in the amount of alcohol vapor added to the aerosol, and therefore affects the instrument response. Several additional forced convection heat transfer CNCs have been released by TSI in recent years. These include higher flow rate instruments designed for monitoring in semiconductor clean rooms, instruments for industrial hygiene applications, instruments with improved response for ultrafine particles, etc.

A number of refinements in the design of continuous flow CNCs have been reported since 1980. J. C. Wilson and coworkers (Wilson et al. 1983a, 1983b) describe an instrument designed to operate in aircraft for studies of stratospheric aerosols. Design priorities included fast time response and the ability to count accurately at low pressures. A schematic of their instrument is shown in Figure 9. Filtered sheath air was used

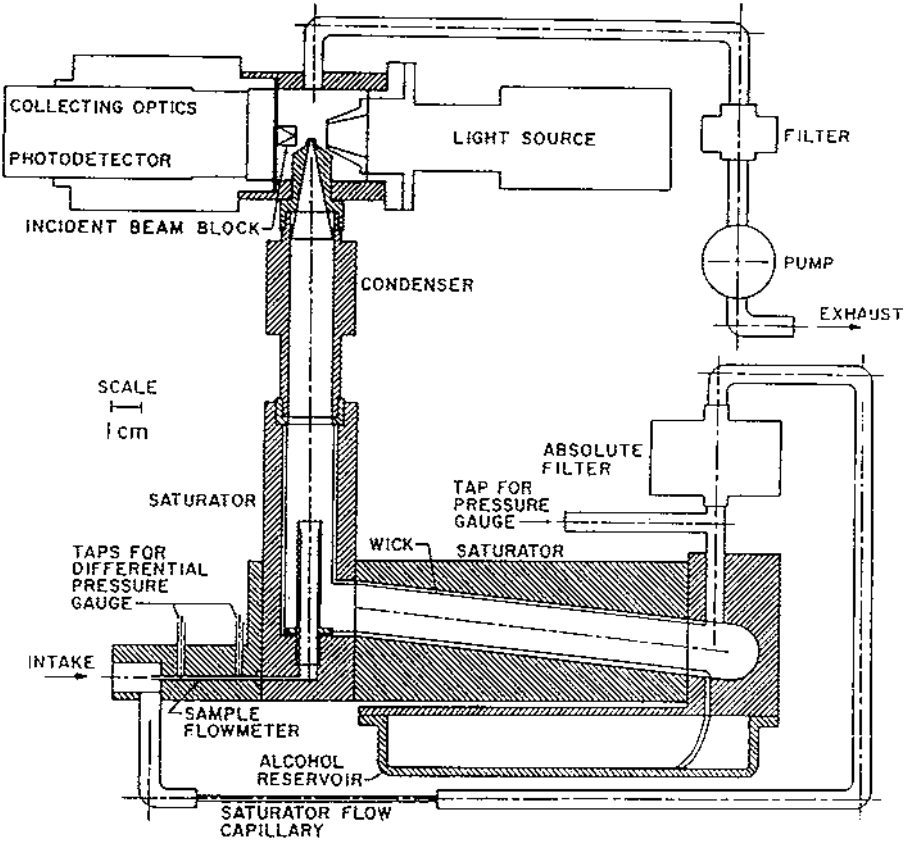

FIGURE 9. Continuous flow, single-particle counting condensation nucleus counter with filtered sheath air for stratospheric aerosol measurements. (J. C. Wilson, J. H. Hyun, and E. D. Blackshear, *J. Geophysical Research*, volume 88:6781–6785, 1983, copyright by the American Geophysical Union.)

to confine aerosol to the center streamline of the condenser, thereby reducing the instrument response time, reducing diffusion losses, and ensuring that all particles were exposed to similar supersaturation profiles as they flowed through the condenser. It was found that the sheath air design reduced the sensitivity of the instrument response to pressure in the 400–40 mbar range (~8–21.5 km). This instrument and its successors have played an important role in NASA's research on stratospheric ozone depletion (e.g., Wilson et al. 1989).

The sheath air design of Wilson and coworkers was used by Stolzenburg and McMurry (1991) in an ultrafine condensation nucleus, which served as the prototype for the TSI 3025. With this instrument, particles of 3 nm are detected with approximately 50% efficiency at one atmosphere pressure; efficiencies drop rapidly to zero for particles smaller than 3 nm. The use of sheath air ensures that all particles are confined to the axis of the condenser where the highest saturation ratios are reached. Diffusional losses through the 2 cm long inlet capillary are small and can be determined theoretically.

Recent work has shown that the prototype instrument of Stolzenburg and McMurry can be used to obtain size distributions of ultrafine aerosols. The sizing scheme is based on the observations of Brockmann (1981) and Stolzenburg (1988) that pulse heights produced by the photodetector of the TSI 3020 decrease with decreasing particle size for particles smaller than 15–20 nm, as shown in Figure 10. They argued that pulse heights decrease with size because, due to the Kelvin effect, smaller particles travel further into the condenser before they are activated and therefore have less time to grow than larger particles. The measurement of 3–10 nm aerosol size distributions by the pulse height analysis technique is discussed by Saros et al. (1996) and Weber et al. (1998), and the application of this technique to studies of nucleation in the troposphere has been discussed by Weber et al. (1995). Pulse height analysis cannot be used with the TSI 3025 because its laser particle detector produces Mie resonances that lead

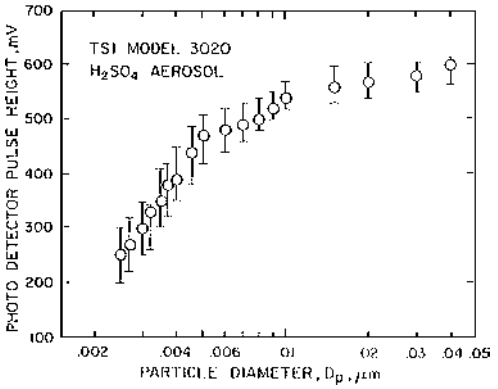

FIGURE 10. Dependence of pulse height on particle size for white light scattered by individual droplets downstream of the condenser in the TSI 3020 CNC (Brockmann 1981).

to a nonmonotonic relationship between particle size and pulse height (Marti et al. 1996).

An alternative scheme for obtaining ultrafine size distributions with a continuous flow CNC was reported by McDermott et al. (1991). These investigators used a sheath air inlet similar to that described by Stolzenburg and McMurry to ensure optimal performance for ultrafine particles. Particle size distributions were obtained by carrying out measurements over a range of condenser temperatures: as the condenser temperature decreases the peak supersaturation increases, thereby decreasing the minimum detectable size. This instrument was designed for use in ultraclean gas systems such as are used in semiconductor processing. In order to increase counting rates the ratio of aerosol to sheath gas flow rates was increased from 1:10 to 1:1 while maintaining a total flow rate of 5.0 cm^3/s. More recently, Mertes et al. (1995) showed that adjusting the temperature difference between the saturator and condenser can vary the minimum detectable size of the TSI 3010 CPC. Brock (1998) developed the nuclei-mode aerosol size spectrometer that utilizes Kelvin-effect sizing to obtain fast-time response (~1 s) measurements of sub 100 nm size distributions in aircraft. This instrument utilizes parallel measurements with

five CNCs having differing minimum detectable sizes.

Mixing-Type CNCs

Holl and Mühleisen (1955) developed a steady-flow condensation nucleus counter used for studies of the relationship between atmospheric conductivity and condensation nuclei concentrations. Unlike other mixing-type CNCs which achieve supersaturation by mixing warm and cool vapor streams, this instrument involves the isothermal mixing of HCl vapor into a chamber that is saturated with water vapor, as shown in Figure 11. Aerosol and HCl vapor enter the chamber at constant flow rates through separate entrances; gas is withdrawn from the chamber through an exit that is connected to a water pump. Although the water vapor and HCl alone are subsaturated under these conditions, the vapor mixture is supersaturated relative to aqueous HCl solutions, and binary condensation on particles occurs. I am not aware of other CNCs that utilize multicomponent condensation.

Another novel mixing-type CNC was described by Cadle and Langer (1975). In this instrument the sampled aerosol was turbulently mixed with filtered moist air at 40°C. Freon was then added to this mixture to cool the flow, thereby causing the water vapor to become supersaturated and condense on particles. The instrument was used for stratospheric aerosol measurements, and the aerosol was pressurized before it entered the condenser so as to enable it to operate at constant pressure. A curious feature of this instrument is its single particle detection scheme shown in Figure 12. At the exit from the condenser, particles flowed through a 6 cm long glass capillary that tapered gradually to 1.5–5.0 mm. A pressure drop of 150 mm Hg leads to a velocity of 50 m/s through the capillary. When particles larger than 20 μm flow through this capillary they produce audible "clicks" that were detected with a microphone.

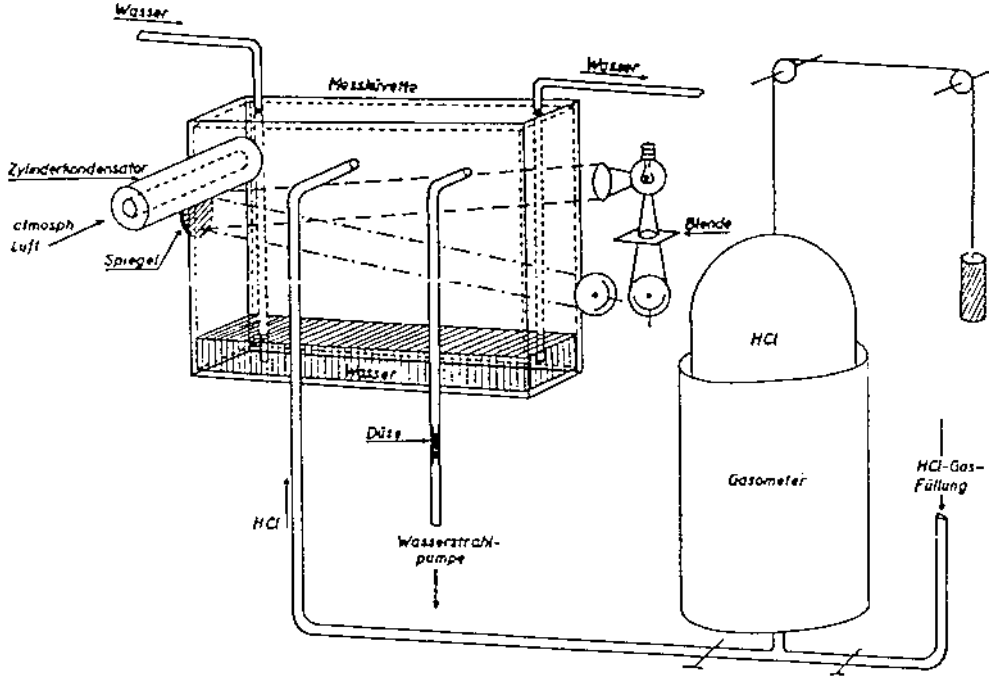

FIGURE 11. Condensation nucleus counter utilizing multicomponent vapor condensation reproduced by permission of Birkhaeuser Publishers Ltd. from *Geofis. Pura Appl.*, volume 31 (1955), pp. 21–25.

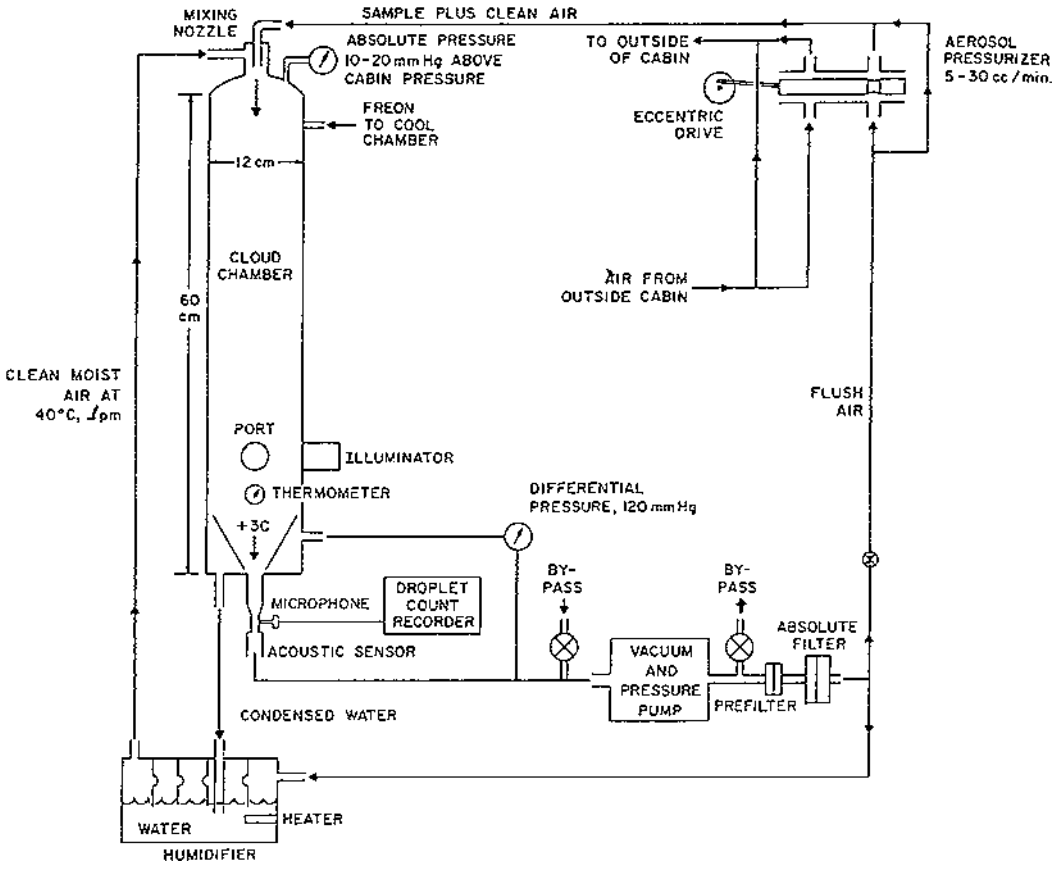

FIGURE 12. Mixing-type CNC with acoustic detector. (R. D. Cadle and G. Langer, *Geophysical Research Letters*, volume 2:329–332, 1975, copyright by the American Geophysical Union.)

Fuchs and coworkers (Fuchs and Sutugin 1965) used a particle size magnifier (PSM) that was developed by Kogan and coworkers. In this instrument, aerosol flowing at 5.1 lpm was mixed with 1.7 lpm of hot nitrogen containing dibutyl phthalate (DBT) vapor. The DBT became supersaturated in the mixed flow and condensed on preexisting particles. The particles grew to ~ 0.3 μm and were manually counted using an ultramicroscope.

Kousaka and coworkers further refined the design of mixing-type CNCs similar to those originally developed in Russia (Yoshida et al. 1976; Kousaka et al. 1982; Okuyama et al. 1984; Kousaka et al. 1992). A schematic diagram of the instrument described in their 1982 paper is shown in Figure 13. Warm and cool streams of aerosol saturated with the working fluid (butanol in this case, although a variety of working fluids including water have been used) are turbulently mixed in a nozzle where the vapor becomes supersaturated and condenses on particles. The particle concentration is determined using a video recorder to monitor the flux of particles through a plane downstream of the nozzle; an automatic counter is used to determine concentrations. With these instruments the choice of working fluid is not as tightly constrained by the vapor diffusivity as with forced convection laminar flow instruments because supersaturation is achieved by mixing and not by thermal conduction through the carrier gas. Furthermore, these

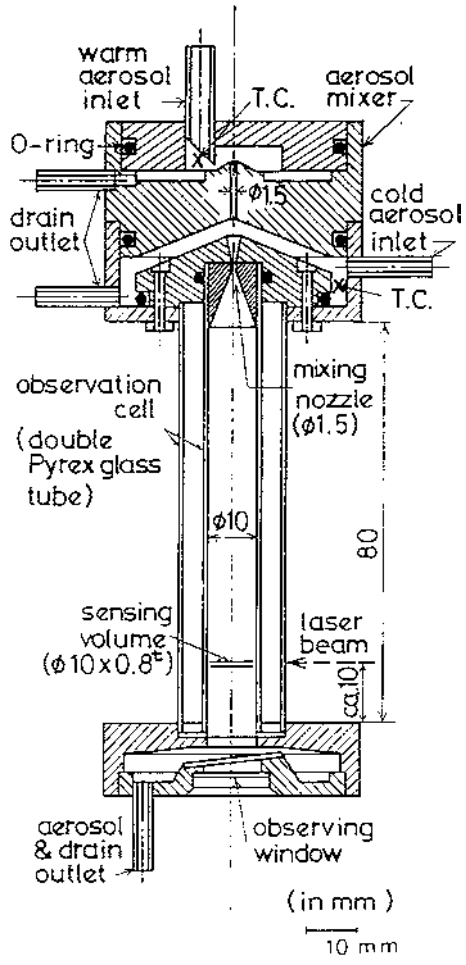

FIGURE 13. Mixing type CNC. Reprinted from the *Journal of Aerosol Science*, volume 13, Y. Kousaka, T. Niida, K. Okuyama, and H. Tanaka, "Development of a mixing type condensation nucleus counter," pp. 231–240, Copyright (1982), with permission from Elsevier Science.

instruments can be designed to detect ultrafine particles with high efficiency (Bartz et al. 1985) and can be scaled to operate over a range of flowrates. The 14 lpm instrument described by Kousaka et al. (1992) is the highest sampling rate CNC that I am aware of. A mixing-type CNC that operates at 0.1 cfm and uses propylene glycol as a working fluid is commercially available from Nihon Kagaku Kogyo Co. (KANOMAX Model 3851).

Fernández de la Mora and coworkers (Seto et al. 1997; Gamero-Castaño and Fernández de la Mora 1999) recently reported on the use of mixing-type CNCs to detect ions produced with an electrospray and size-classified with a high-resolution electrical mobility analyzer. They were able to detect charged subnanometer particles (ions) with "effectively no lower size limit." This technique is beginning to provide important new information on ion induced nucleation.

Segmented Thermal Diffusion Chamber

Hoppel et al. (1979) reported on the design and performance of a segmented thermal diffusion CNC. They built this instrument in response to their need for a steady-flow detector downstream of an electrostatic classifier (Hoppel 1978). A schematic of the segmented thermal diffusion CNC is shown in Figure 14. It consists of a vertical cylindrical tube with hot and cold segments that are saturated with water. The aerosol transport time through a single hot or cold segment is short relative to time required to reach thermal equilibrium or vapor-liquid equilibrium. The total flow time through the tube, however, is long relative to time for lateral diffusion or heat transfer. Under these conditions it can be shown that the temperature and vapor concentration along the axis achieve values that are intermediate to the temperature and vapor pressure of the hot and cold segments. Because of the exponential increase of equilibrium vapor pressure with temperature, the vapor along the axis is supersaturated at the exit from the system. The grown particles are detected with an optical particle counter.

CNC CALIBRATION

A history of CNCs would be incomplete without a discussion of instrument calibration. The early instruments all involved manual counting of the number of droplets in a known volume of air, and this provided an absolute visual determination of the particle number concentration.

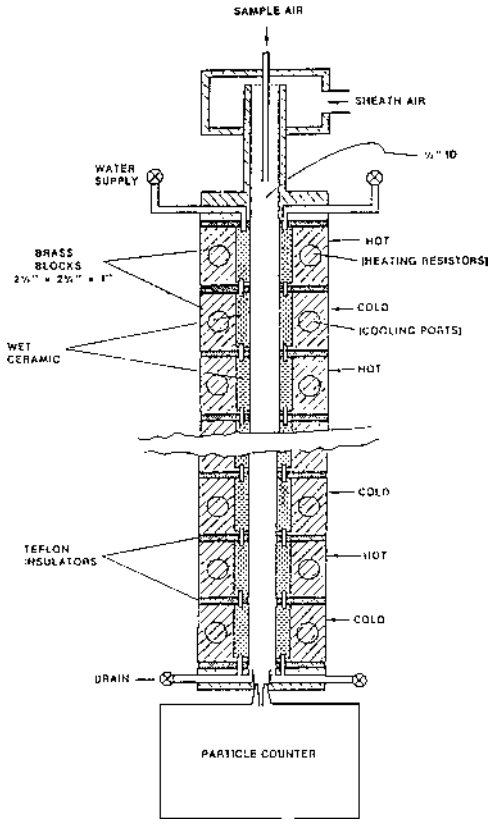

FIGURE 14. Steady flow segmented thermal diffusion chamber. Reprinted from the *Journal of Aerosol Science*, volume 10, W. A. Hoppel, S. Twomey, and T. A. Wojciechowski, "A segmented thermal diffusion chamber for continuous measurements of CN," pp. 369–373, Copyright (1979), with permission from Elsevier Science.

However, even with this seemingly foolproof approach ambiguities were reported. It was observed, for example, that if the aerosol in a chamber was expanded more than once, particles were typically detected after the first expansion even though sufficient time was provided for all droplets to settle out. Landsberg (1938) summarized the arguments of numerous investigators as to whether the true concentration is obtained from the first expansion or is obtained by adding up the total concentration that is observed in a succession of expansions. It was his conclusion that the results of multiple expansions should be added, although this does not conform to the usual practice followed with these instruments. Calibration of photoelectric detectors is even more critical, since there is no simple relationship between concentration and attenuation.

There are two major milestones in CNC calibration. The first of these is the "Tube-Bridge" used by Nolan and Pollak (1946). The Tube-Bridge, as shown in Figure 15, consisted of two parallel flow paths, A and B, each of which contained a pair of 73 cm long, 3 mm i.d. steel tubes. The stopcock P in path B was adjusted so that the pressure drop across it was equal to the pressure drop across the filter, F. This ensured that the flow rates through tubes 3 and 4 were equal and that half of the flow passed through the filter. Because diffusional losses in paths A and B were equal, it follows that the concentration

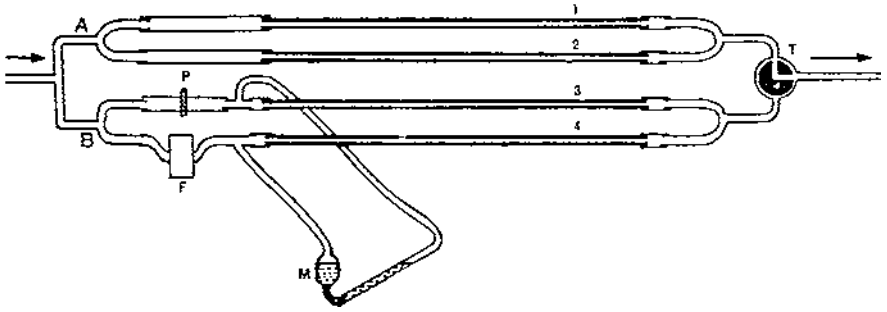

FIGURE 15. Tube bridge for calibrating expansion-type photoelectric CNCs. Reproduced by permission of the Royal Irish Academy from *Proceedingss of the Royal Irish Academy*, volume 4 (1946), pp. 161–180.

downstream of path B is one half the concentration downstream of path A.

In using the Tube-Bridge to calibrate a photoelectric counter, a flask was first filled with aerosol from a Bunsen burner. The counter was then used to measure the aerosol downstream of paths A and B. A succession of measurements of this type was made as time progressed and the aerosol concentration in the flask decreased by coagulation and deposition. By this means (Nolan 1972) "a series of pairs of extinction values E and e is obtained, each pair corresponding to a certain (so far unknown) concentration of nuclei and to half that concentration." After some time concentrations in the flask decreased sufficiently to permit the measurement of the "absolute" concentration using an Aitken pocket counter. The Aitken pocket counter measurement "anchored" the bottom of the photoelectric counter calibration curve. With this plus the Tube-Bridge data it was possible to determine the attenuation corresponding to twice that concentration, etc., thereby working up to arbitrarily high values. This scheme provided the primary calibration for the Pollak counters that were used as secondary calibration standards for CNCs for the next 30 years.

The second major milestone in CNC calibration involves the use of an aerosol electrometer and differential mobility analyzer (AE/DMA)

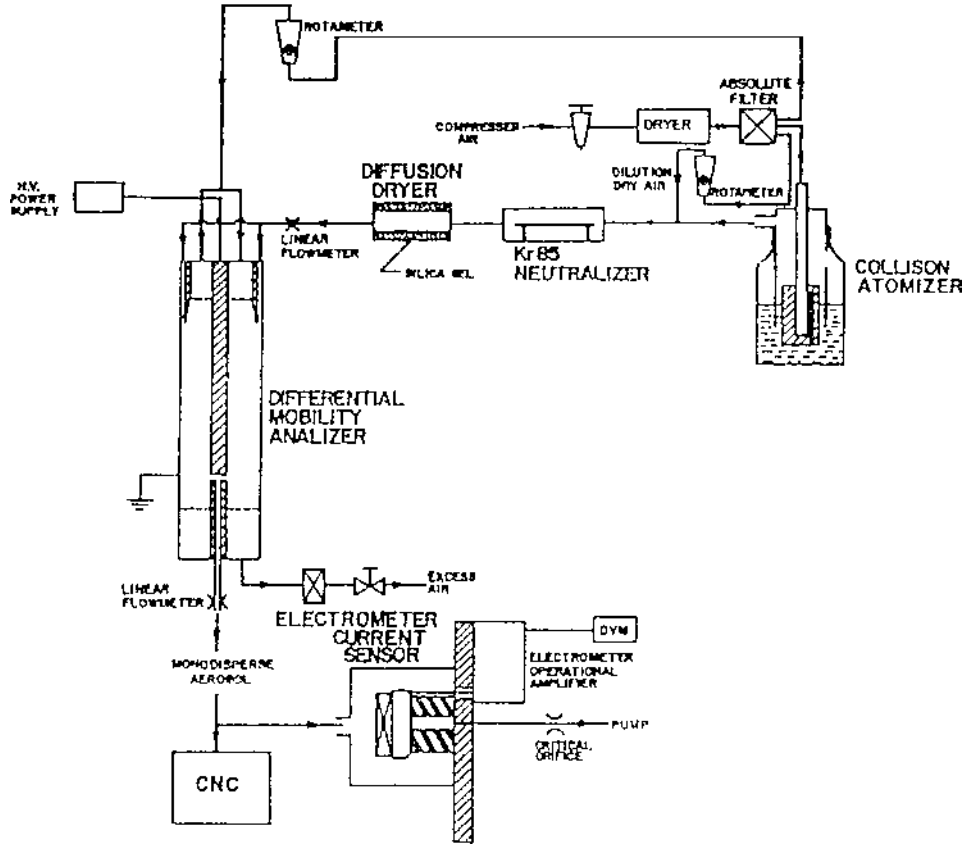

FIGURE 16. The differential mobility analyzer and aerosol electrometer used to produce calibration aerosols of known size, composition, and concentration. (Republished with permission of the *Journal of Colloid and Interface Science* from "A submicron aerosol standard and the primary, absolute calibration of the condensation nuclei counter," by B. Y. H. Liu and D. Y. H. Pui, volume 47, pp. 155–171, 1974, conveyed through Copyright Clearance Center, Inc.)

first reported by Liu and Pui (1974) in their paper on the "primary, absolute calibration of the condensation nuclei counter." A schematic diagram of their calibration system is shown in Figure 16. The electrostatic classifier (Knutson and Whitby 1975) is used to deliver singly-charged, monodisperse calibration aerosols of known size and composition. The aerosol electrometer and CNC sample this aerosol in parallel downstream of the classifier. The "true" concentration, N_{ae}, is obtained from the aerosol electrometer current, I, using the following relationship:

$$N_{ae} = \frac{I}{Q \cdot e},$$

where Q is the volumetric flow rate through the aerosol electrometer and e is the charge per electron. Advantages of the AE/DMA technique are that it provides an independent measurement scheme that does not rely on condensation and it enables measurements with monodisperse particles of known size and compostion. The primary complication is that multiply charged particles having the same mobility as the desired singly charged particles may be included with the aerosol leaving the DMA, leading to a more complicated relationship between current and concentration. In this first study Liu and Pui found that an Environment/One Model Rich 100 indicated concentrations that were a factor of 2.5 lower than those indicated by the aerosol electrometer. Smaller but significant discrepancies were found between the AE/DMA and a GE CNC.

In a subsequent study the AE/DMA method was used to evaluate the calibration of the Pollak Model 1957 (Liu et al. 1975). They found that the Model 1957 agreed with the aerosol electrometer to within 9% for concentrations between 10^2 and 10^4 cm^3 and within 17% for concentrations up to 2.5×10^5 cm^{-3}. The agreement between these independent measurement methods supported the validity of Pollak's careful work and led to widespread acceptance of the AE/DMA technique. Since this time the AE/DMA approach has been adopted as a calibration standard in many laboratories and in numerous calibration workshops (e.g., Liu et al. 1982; Bartz et al. 1985; Wiedensohler et al. 1997).

An unexpected outcome of calibrations done with the AE/DMA method was the observed dependence of CNC counting efficiency on particle size for very small particles. Up until this time it had been widely believed that the minimum detectable size was about 2 nm and that 100% of the particles down to this size were detected. The minimum detectable sizes were determined from the Kelvin-equivalent size that could be activated for the supersaturations that were achieved at the CNC expansion ratio. As shown in Figure 17, Liu and Kim (1977) showed that contrary to expectations the counting efficiency of the GE CNC decreased sharply with size for particles smaller

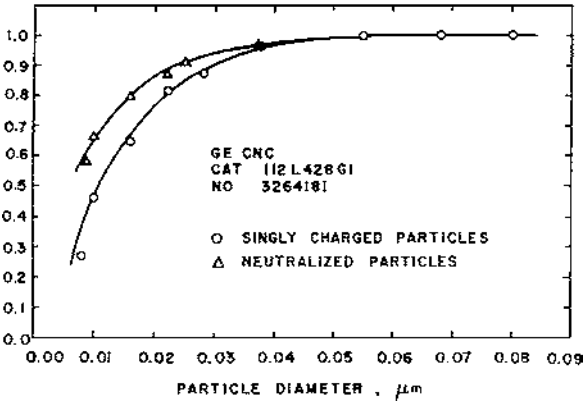

FIGURE 17. Dependence of counting efficiency on particle size for the GE CNC. Reprinted from *Atmospheric Environment*, volume 11, B. Y. H. Liu and C. S. Kim, "On the counting efficiency of condensation nuclei counters," pp. 1097–1100, Copyright (1977), with permission from Elsevier Science.

than 40 nm. Shortly thereafter many other investigators found similar results for other instruments of both the expansion and steady-flow type. The fact that counting efficiencies depend on instrument design is now widely accepted. Factors that influence counting efficiency include diffusional deposition in the inlet and variations in the saturation ratio profile within the instrument.

SUMMARY

Figure 18 provides a timeline of key developments in the history of CNCs. This history separates into two distinct phases. Virtually all of the work before 1970 utilized expansion-type instruments with water as the working fluid. Since 1970, steady-flow instruments that utilize a variety of working fluids have evolved into the most commonly used CNCs. The steady flow instruments have grown in favor due to 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.

The development of the electrostatic classifier led to a quantum improvement in our

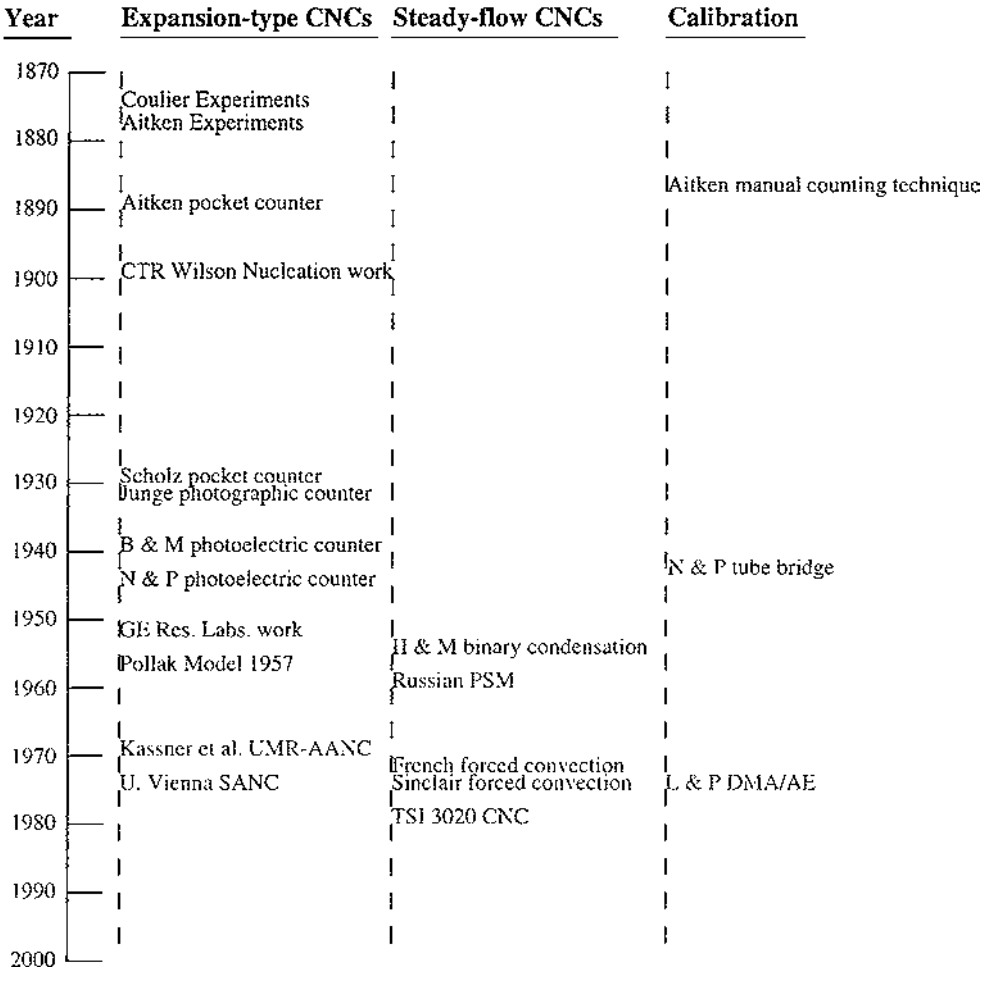

FIGURE 18. Timeline summarizing major milestones in the development of CNCs.

understanding of CNC performance. This provided calibration aerosols of known size, charge, and composition, and with the aerosol electrometer provided a concentration standard that does not utilize condensation. This approach led to important discoveries about the dependence of CNC response on particle size in the nanometer range and since the mid 1970s has been a component of most CNC intercomparison studies.

This paper would not have been written without the encouragement of Gil Sem, who invited me to present a lecture on this subject at the 1993 meeting of the American Association for Aerosol Research. I also appreciate the information provided by Barry Bodhaine, Robert Gussman, Austin Hogan, Ruprecht Jaenicke, Volker Mohnen, and George Skala through letters or conversation.

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