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COMPARISON OF SEVERAL AITKEN NUCLEI COUNTERS

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Abstract—The basic thermodynamical processes leading to the formation of droplets in the central part of the Nolan–Pollak counter are analyzed in some detail. The comparison of the UMR–Absolute Aitken Nuclei counter with Nolan–Pollak, General Electric and Gardner counters showed consistently higher counts of the UMR–AAN counter. The mean deviations varied between 20% and 50% depending on the type of the counter, nuclei concentration and nature. Several observations are made on ultrafine particle counting.

INTRODUCTION

The history of the term ‘Aitken nuclei’ antedates its namesake by thirty years with the work of Becquerel who, around 1837, stressed the important role of tiny dust particles in the condensation process. More than thirty years later Aitken tried to explain the origin of fog and cloud droplets in connection with his measurements of condensation nuclei with his ‘pocket counter’. Aitken demonstrated clearly how nuclei of different concentration or of different nature produced cloud. It was not until 1941 that Sir George Simpson expressed serious doubt about the applicability of measurements using counters of the Aitken type for the quantitative explanation of cloud formation in the atmosphere. His doubt arose from the analyses of nuclei activation and droplet growth in natural clouds as opposed to clouds produced inside the counter. Since that time it is conventional to distinguish between those nuclei activated at the very high supersaturations produced in the AN counter ($> 200\%$) and those active at naturally produced supersaturations ($< 1\%$). The first group included, at least ideally, all particles activated (and presumably counted) up to the critical supersaturation corresponding to the condensation of water vapor on light ions ($\sim 350\%$). The second group, active at much lower supersaturations, were called cloud condensation nuclei (CCN). It is in this way that one conventionally expresses the distinction between the totality of airborne particles and those specifically active in the formation of natural clouds.

The world-wide collection of AN data prior to World War II was obtained by using counters based on the operational principles of Aitken’s pocket counter (Burckhardt and Flohn, 1939; Landsberg, 1938). These expansion type counters (Aitken or Scholtz) were later largely superseded by the more convenient ‘relative’ counters. In the latter instruments the tedious counting of drops was replaced by the measurement of light extinction produced by the drop population, and a concentration inferred from that measurement. The extinction technique, being less direct, gave rise to the name ‘relative’ counter. Throughout the following text

we will use for the ‘pocket’ type counters and all counters based on a direct counting of droplets (but indirect counting of nuclei) the name of an ‘absolute counter’ as was suggested by Pollak (1959).

‘Relative’ counters are mainly represented by the photoelectric Nolan–Pollak (N–P) counter (some authors prefer to use the name of Pollak counter) which evolved over two decades of very careful and systematic experiments (Pollak, 1959; Pollak and Metnieks, 1957, 1959, 1960, 1961). Due to its simple operation and high reproducibility N–P counter—originally calibrated by an Aitken counter and later by Scholz counter—was selected by many investigators as a secondary standard.

The principles of N–P counter were used in the Gardner counter and in several types of automatic condensation nuclei counters (Verzar’s, GE and Environment One counters). The fast cycling of the expansion and humidification of the air sample in an automatic counter enabled one to obtain a continuous record but at the price of introducing a new largely unknown parameters: the particle response (relaxation) time to the rapidly changing environment. Recently a more sophisticated counter measuring and recording optical parameters of droplets growing on sampled nuclei was described and used by Wagner (1974).

The evolution of ‘absolute’ AN counters lagged the rapid development and use of ‘relative’ counters. Direct photographing of droplets in the counter’s sensitive volume was suggested by Junge in 1961 and later by Käselau *et al.* (1974) and used for balloon borne instruments. The so called UMR Absolute Aitken Nuclei Counter (UMR–AANC; Kassner *et al.*, 1968) consists basically of a large Wilson type expansion chamber with piston under water surface. The chamber stores 15 l of clean air which is mixed with sampled nuclei-laden air and can be operated automatically at supersaturations ranging from 24 to 380%. The droplets formed on nuclei are directly photographed in the counter. Direct photography of droplets and the use of ‘out-of-focus method’ for evaluation of the photographs is also employed in

Kanter counter (Kanter and Junge, 1971) and in a more advanced version which uses air expansion (pressure expansion ratio 1.21) in a cylindrical chamber of 359 cm³ sensitive volume and 4.0 cm inner diameter (Jaenicke and Kanter, 1976).

Several investigators started to use vapours of liquids other than water for the total submicron particle (condensation nuclei) detection (Bricard *et al.*, 1972; Rosen *et al.*, 1974). There is no fundamental objection to the use of other liquids; however, it would be necessary to calibrate such counters by using a great variety of nuclei and a wide range of nuclei concentrations before converting the numbers of nuclei (CN) measured in this manner into AN concentrations.

Large numbers of instruments measuring AN or total number of submicron particles suggested several times in history the idea of a comparison by using a well defined aerosol. Several problems of AN counter comparison were discussed during the first International Workshop on Condensation and Ice Nuclei at Lannemezan in 1967. During the second workshop at Fort Collins in 1970 a direct comparison of AN counter was made; however, several results of this comparison were rather inconclusive (Grant, 1971). Later an attempt to compare several AN counters with the UMR-AANC led to the conclusion that this instrument counts higher concentrations than the other counters based largely on the previous comparison with N-P counter. A systematic comparison of CN counters at Boulder in 1974 (Cadle *et al.*, 1975) showed that N-P counter, special type of General Electric counter (SANDS) and Rosen-Hoffman counter correspond well in the range of CN concentrations between 100 and 10,000 CN cm⁻³ and that Langer CN counter recorded systematically lower counts. However, most of the test aerosol particles used had sizes larger than 0.05 μm. An indirect comparison with the UMR-AANC led Podzimek and Kassner (1976) to the conclusion that all counters compared at Boulder to the N-P counter count lower CN concentrations. This difference could amount to 30% of the measured CN concentration.

Among the AN comparisons involving several counters one can mention the calibration of N-P counter with monodisperse aerosols and comparison with an Electrical Aerosol Detector (Liu *et al.*, 1975), calibration of the Stratospheric AN Detection System (SANDS) with UMR-AANC (Wegrzyn and Podzimek, 1975) and comparison of a Small Scholz counter with another 'absolute' counter (Jaenicke and Kanter, 1976). The comparison *in situ* of an 'absolute' Kanter AN counter with a 'relative' Rosen and Hoffman counter (Rosen *et al.*, 1978) left unexplained a number of deviations of individual simultaneous measurements in spite of a similar trend of the counts of both instruments. The last comparison of several AN counters in Vienna (Preining *et al.*, 1979) included Size Analyzing Nucleus Counter (SANC) built in Vienna (Wagner, 1974), TSI-Condensation Nucleus Counter and Jaenicke-CN counter (Jaenicke

and Kanter, 1976). Comparison was also made with an Electrostatic Classifier (TSI) and Aerosol Electrometer (TSI). Sodium chloride particles of diameter of 0.056 μm were used for counter comparison in concentration range 300–300,000 cm⁻³. For special droplet growth studies DOP and NaCl aerosol of diameters 0.01–0.1 μm and 0.56 μm were vented into the SANC. The comparison of all counters with the Aerosol Electrometer showed that the TSI instruments recorded systematically higher counts than SANC and Jaenicke counter. At CN concentrations larger than 10,000 cm⁻³ this difference was around 40%. However, at concentrations smaller than 5000 CN cm⁻³ the Jaenicke counter indicated CN concentrations slightly lower (8–15%) than the TSI instruments whereas SANC recorded consistently lower counts of about 40%.

Similar discrepancies characterized almost all AN (or CN, if other vapors than water vapor were used) counter comparisons in the past, particularly those which were motivated by the use of AN counters in environmental studies. A successful application of AN counters in the field, however, assumed that one possessed answers to several important questions, such as the comparability of CN counters based on different principles in different CN concentration and size range. One raised the question as to what extent the AN (CN) counter can be considered as a total particle (number) counter with regard to particle nature and different threshold of particle size detectability in a specific counter. Finally, one attempts to establish simple models describing the particle behavior in an AN counter and to explain some of the observed discrepancies during AN counter calibration.

The authors had the same questions in mind when a one year program of AN counter comparison started at the Graduate Center for Cloud Physics Research of the University of Missouri-Rolla in 1978. The main goal of the program supported by the U.S. Department of Transportation was to compare several commercially produced AN counters with the UMR-AANC and to point out features of a specific counter important for its use. Other relevant questions such as particle losses during the storage, sampling and measurement, expansion counter comparison with other counting techniques and the potential particle size threshold of nuclei counted in AN counters were discussed elsewhere (Podzimek *et al.*, 1980).

METHODOLOGY OF AITKEN NUCLEI COUNTING

We have chosen to model the N-P counter both because it typifies the expansion type and it is generally regarded as the most reliable of its kind. In this study we will model its 'ideal' behavior, that is we confine our attention to that interval of time between the end of the pressure expansion and the beginning of that regime where heat from the side walls reaches the central illuminated volume. Thus 'ideal' behavior may be

characterized by an instantaneous (but nevertheless isentropic) pressure drop to 1 atmosphere with no side wall heating. The major assumption of the model is that the drop size distribution is monodisperse. With these simplifications the model appeals to the calculation of isolated cloud growth already available (Carstens, 1979).

Standard pre-expansion conditions in the N-P counter are as follows: temperature, 20°C; pressure, 1.21 atm.; supersaturation ratio, 1.0. These conditions imply an ideal operating supersaturation ratio of 2.3 and a minimum dry adiabatic temperature of 4.46°C. As is well known the wet bulb temperature is calculated from two distinct points of view: (a) directly from its physical interpretation as the final equilibrium temperature achieved by an isolated system that is initially supersaturated, and (b) indirectly, as the surface temperature of a wet bulb immersed within the air-water-vapor system in this case a drop of radius a . The two formulations give (respectively) the following two equations:

$$e_{\text{eq}}(T_f) - e^{(0)} = -\frac{C_p p}{\varepsilon L} (T_f - T^{(0)}) \quad (1)$$

where $e_{\text{eq}}(T_f)$ is the equilibrium water vapor pressure at the wet-bulb temperature T_f , and

$$\frac{e_A - e_{\text{eq}}(T_a)}{T_a - T_A} = \frac{K p}{\varepsilon L \rho D} = \Gamma \quad (2)$$

where $T_a \approx T_f$. Here p is the total pressure (10^3 mb), $\varepsilon = M_v/M_g = 0.66214$, $C_p = 0.24$ cal $\text{g}^{-1} \text{C}^{-1}$, $L = 595$ cal g^{-1} , $D = 0.204$ $\text{cm}^2 \text{s}^{-1}$ and $K = 5.86 \times 10^{-5}$ cal $\text{s}^{-1} \text{cm}^{-1} \text{C}^{-1}$ (D and K are from Beard and Pruppacher, 1971), and $\rho =$ gas density. The superscript "0" denotes initial conditions, and the subscript "A" denotes ambient values. At 10°C one obtains $\Gamma = 0.61$ and $T_a = 12.45^\circ\text{C}$. The fact that $T_a \approx T_f$ allows us to approximate saturation conditions at the drop surface throughout the process by a simple linear relation,

$$e_{\text{eq}}(T_a) = B T_a + C$$

where for the conditions contemplated here we take $B = 0.9425$ $\text{mb}^\circ\text{C}^{-1}$ and $C = -254.75$ mb.

It is convenient at this point to introduce the cellular model wherein each drop is surrounded by a concentric sphere of radius A ($A \gg a$) which is impermeable to both vapor and heat. The cell so defined allots to each drop its share of vapor and provides it a finite heat sink as well. The cell radius is chosen so as to fill all space, i.e.

$$\frac{4}{3} \pi A^3 N = 1$$

where N is the drop concentration. In terms of this cellular model the growth equation for an isolated, monodisperse cloud is (Carstens, 1979)

$$(a+l) \frac{da}{dt} = \Lambda D_{\text{eff}} \left[\left(\frac{a_\infty}{A} \right)^3 - \left(\frac{a}{A} \right)^3 \right] \quad (3)$$

where a_∞ represents the final radius,

$$\left(\frac{a_\infty}{A} \right)^3 = \frac{e_A^{(0)} - (B T_A^{(0)} + C)}{\sigma \kappa \left[e_A^{(0)} + \frac{T_A^{(0)}}{\kappa} - C \right]}$$

$\sigma = R \rho_l / M_v$, $\kappa = \frac{L M_v}{p C_p M_g}$, $\rho_l =$ liquid density, $M_v =$ molecular weight of vapor (M_g that of carrier gas)

$$D_{\text{eff}} = \left(\frac{1}{D} + \frac{B L M_v}{K R T} \right)^{-1}$$

$$\Lambda = 1 + \kappa B \frac{T_f}{T_A^{(0)}} + \kappa \left(\frac{e_A^{(0)} - e_{\text{eq}}(T_f)}{T_A^{(0)}} \right)$$

The parameter l accounts for the retarding effects associated with the liquid-gas interface, namely sticking of vapor molecules and thermal accommodation of the gas molecules (Carstens, 1979). We here adopt the value $\alpha = 1$ so that, under N-P counter conditions we have

$$l = 0.0562 \frac{1 - \beta/2}{\beta} + 0.757.$$

Often the coefficient $\frac{1 - \beta/2}{\beta}$ is replaced by β^{-1} simply,

and we have chosen to vary the coefficient $\frac{1 - \beta/2}{\beta}$ from 0.01 to 1. (Note that the absurd value of zero for this last coefficient corresponds to transport which is entirely diffusively controlled.)

The solution to Equation (3) may be written

$$\frac{t}{\tau} = \frac{1 - l/a_\infty}{1 + l/a_\infty} f_1 + f_2$$

where

$$\tau = \tau_0 (1 + l/a_\infty), \quad \tau_0 = \frac{A^3}{3 a_\infty \Lambda D_{\text{eff}}}$$

and

$$f_1 = \sqrt{3} \left[\frac{\pi}{6} - \tan^{-1} \frac{2 \frac{a}{a_\infty} + 1}{\sqrt{3}} \right],$$

$$f_2 = \frac{1}{2} \ln \left[\frac{1 + a/a_\infty + a^2/a_\infty^2}{(1 - a/a_\infty)^2} \right].$$

τ , the relaxation time, can be chosen in accordance with the criterion that, as $a \rightarrow a_\infty$, the dominant term in $t(a)$ is $\ln(1 - a/a_\infty)$, i.e.

$$a \sim a_\infty \exp(-t/\tau),$$

for $a \rightarrow a_\infty$.

Figure 1 displays a plot of droplet radius and characteristic time τ_0 for various AN concentrations. The calculations reveal, for example, that at very low nuclei concentrations (e.g. encountered in remote areas over the ocean) the nuclei give rise to droplets which

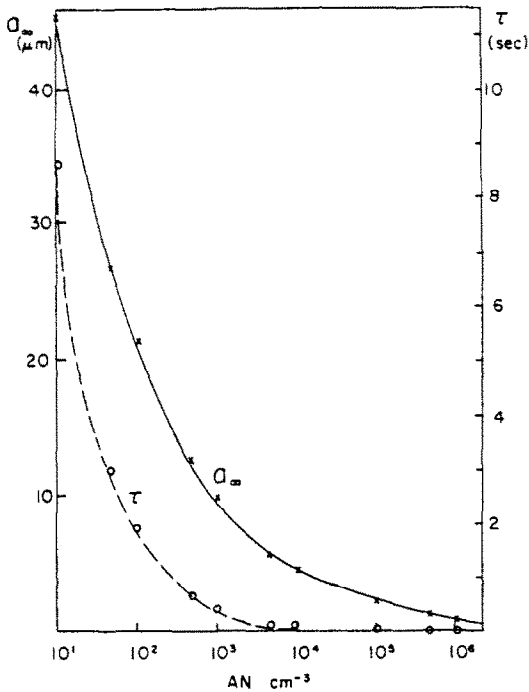


Fig. 1. Final radii a_x (μm) and characteristic time τ (s) for various drop concentrations.

grow to sizes exceeding $10\ \mu\text{m}$ in times, τ_0 , surpassing 1 s. Also shown are the results of such calculations for concentrations of 10^2 and $10^3\ \text{cm}^{-3}$ for various values of the sticking coefficient β (Fig. 2). Simple relations are seen to exist between a_x , τ_0 , and AN concentration, N , namely:

$$a_x \cong 10^2/N^{1.3},$$

$$\tau_0 \cong 40/N^{2.3}.$$

Furthermore, the effect of β is not strong if its value is greater than 0.03 at least for reasonably high concentrations. However at low concentrations con-

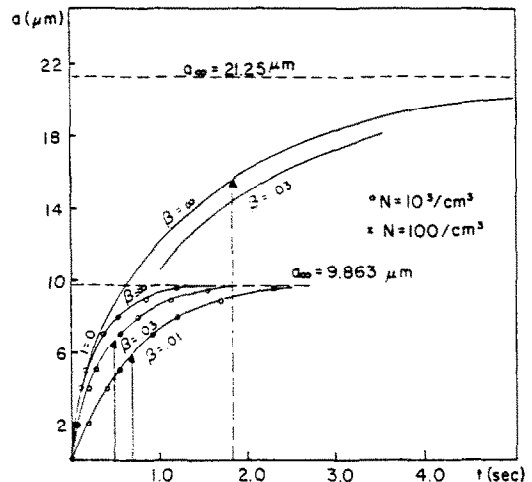


Fig. 2. Droplet radius a (μm) vs time for $N = 10^2\ \text{cm}^{-3}$ and $10^3\ \text{cm}^{-3}$ and different values of β (0.01; 0.03; ∞).

sideration must be given to the possibility that growth to near a_x may be prolonged. This may be a problem in fast cycling expansion chambers where drops never achieve a 'final' radius.

EXPERIMENTAL SETUP

AN counters, were calibrated in the air-conditioned laboratory of the Graduate Center for Cloud Physics Research, UMR, in the spring, summer and fall of 1979. Figure 3 shows the setup of AN counter comparison. The UMR-AAN and N-P counters are connected with 2.0 m long tygon tube of 1.0 cm I.D. with the storage mylar bag of 0.5 or 15.0 m^3 volume in a metallic chamber with adjustable inner pressure. GA and GE counters were connected with a 1.5 m long tygon tube of 1.0 cm I.D. to the same storage bag. The Precision Pressure Gage (Texas Instruments, Inc. Model 145) served as a reference pressure instrument.

Technical data of the compared counters are contained in Table 1.

Table 1

Type of counter	Principle of AN counting	Sensit. volume. (surf. area/volume ratio)	Expansion pressure ratio (supersaturation)	AN concn range (cm^{-3})	Accuracy (%)
Gardner Counter Cat. 70,004G-2 Ser. 1250, year 1978	Light extinction	150 cm^3 (1.68 cm^{-1})	1.151 (1.134)	200 to over 100,000	± 20
N-P Counter Mod. 186922 (1957) Mod. 186920	Light extinction	208.5 cm^3 (1.63 cm^{-1})	1.21 (1.30)	100 to 500,000	± 16
UMR-ANN Counter	Droplet photography	15,000 cm^3 (0.23 cm^{-1})	1.33 (2.45)	10 to over 10,000,000 (with dilution)	± 15
GE-CN Counter No. 112L2861	Light scattering	20 cm^3	1.27 (1.91)	300 to 10,000,000	± 20

The experiment setup (Fig. 3) was adapted to the final goals of AN counter comparison, namely to compare counters with different aerosol of particle sizes between 0.01 and 1.0 μm and concentrations ranging from 50 to 10^5 AN cm^{-3} . Finally, five different aerosols were selected representing both hygroscopic particles [NaCl , $(\text{NH}_4)_2\text{SO}_4$] and nonhygroscopic particulates (Ni-Cr wire, carbon). In addition, room aerosol representing a mixture of particulates of different origin was used for concentrations up to 8000cm^{-3} .

There were several important questions pertaining to the aerosol generation, storage and sampling. Monodispersity of aerosol was not especially stressed in this study because it is not relevant to AN counting in nature. However, an attempt has been made to keep the AN size distribution reasonably narrow. A wide range of AN concentrations required special techniques for aerosol generation, storage and sampling. For particle counts higher than $10,000$ AN cm^{-3} a direct venting of particles into the counter was used, unfortunately, at the price of higher aerosol variability. This necessitated taking of several measurements at a specific AN concentration in all compared counters during time intervals shorter than 10 min. Calibration with particle concentrations smaller than $10,000$ AN cm^{-3} have been performed usually with aerosols aged for several hours in mylar bags. A detailed investigation of the change in NaCl aerosol size distribution during aerosol storage in a 0.5 m^3 mylar bag showed that a representative sample could be taken 1.5 h after venting the aerosol into the bag. The aerosol was prepared in a way which will be described later and its initial concentration was around $3.0 \times 10^4\text{ cm}^{-3}$ (Podzimek *et al.*, 1980, p. 67).

A rough estimate of main particle losses in the connecting tubes of different lengths was made neglecting minor particle losses (in entrances, valves and fittings) using the Gormley and Kennedy (1949) formula. The results of a simple calculation performed for particles within the size range between 5.0×10^{-7} and $2.0 \times 10^{-5}\text{ cm}$ led to the maximal difference of 1.0% in diffusional particle losses. This justifies the neglect of a possible correction (Podzimek *et al.*, 1980, p. 49).

Tset aerosol was generated in the following ways:

(a) Sodium chloride and ammonium sulfate aerosol was prepared from a salt solution (0.01% by weight) by means of atomization. An atomizer, Model 7300 produced by Environmental Research Corporation with a collision flow of 4 LPM and a filtered air dilution flow of 2.7 LPM is used to generate small droplets. The output concentration was nearly $300,000\text{ cm}^{-3}$ as measured by the Gardner counter (GA). Particle size distribution of both aerosols obtained from electronmicrographs is presented in Fig. 4. An analysis of electronmicrograph pictures support the conclusion that some of the aerosol after they had passed through the diffusional dryer did not crystallize completely and preserve a spherical shape. As shown in Fig. 4, 85% of sodium chloride aerosol contains particles within the diameter range of 0.03 to $0.09\text{ }\mu\text{m}$ and 90% of ammonium sulfate aerosol has particle

sizes between 0.03 and $0.10\text{ }\mu\text{m}$. Particle cumulative size distribution in Fig. 4 represents the number of particles larger than a certain size assuming a normal size distribution of particulates. However, at least 85% of the particles fits better to a lognormal distribution function. For some special studies a NaCl aerosol was generated by the evaporation-condensation technique with one or more furnaces in series, which yielded particles with a median diameter around $0.05\text{ }\mu\text{m}$.

(b) The nonhygroscopic aerosol was generated by electrically heating a nichrome wire coil placed in a Pyrex glass tube. The aerosol was carried to the storage bag by nitrogen gas through a Kr-85-2 mC charge neutralizer (3M Company). From orientational measurements with TSI screen diffusion battery one concludes that the majority of particles generated in this way have diameters smaller than $0.01\text{ }\mu\text{m}$. Larger particles deposited in TSI Electrostatic Precipitator and evaluated in electronmicroscopic pictures show chain-like structure and larger irregular aggregates. The initial concentration of this aerosol was usually of the order of 10^4 particles cm^{-3} .

(c) Carbon aerosol was obtained by evaporation of carbon rods in a machine used for coating electron microscopic samples. An electric current of 36 amps at 5 VAC was used to heat the contiguous points. Among the vast majority of small particles with diameters of 0.002 to $0.02\text{ }\mu\text{m}$ (Fig. 4) were always found several large agglomerates which formed despite the immediate dilution of the aerosol containing air with nitrogen gas. The size distribution of an aged carbon aerosol (more than 24 h) depicted in Fig. 4 might be distorted because of the low efficiency of the electrostatic precipitator for collecting particles with diameters smaller than $0.01\text{ }\mu\text{m}$. An evaluation of electronmicrographs of the freshly generated carbon aerosol shows the median diameter is around $0.15\text{ }\mu\text{m}$.

(d) Room aerosol was sampled in the laboratory and particle size analysis has been performed by Mr. M. Jones with the use of TSI Screen Diffusion Battery. The results depicted in Fig. 5 show a high degree of reproducibility and correspond closely to the simultaneous particle deposition in a 'classical' parallel plate diffusion battery designed by Mr. T. Rich. There is a systematic difference between the size distribution of room aerosol passing through a neutralizer before entering a diffusion battery and particles passing straight into a battery and then into an AN counter. The room aerosol, with concentrations ranging from 4000 cm^{-3} to 8000 cm^{-3} , contains many very small particles with median diameters around $0.020\text{ }\mu\text{m}$. Figure 5 supports the idea that the size distribution of room air aerosol follows approximately the log-normal distribution.

The Kr-85 neutralizer was used in all cases when aerosol generating technique could lead to the electrical charging of particulates and excessive deposition namely in tygon tubes. This was true in the case of nonhygroscopic aerosol such as

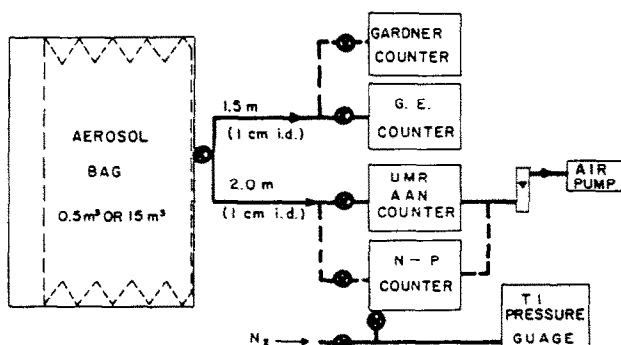


Fig. 3. Experiment setup of AN counter comparison.

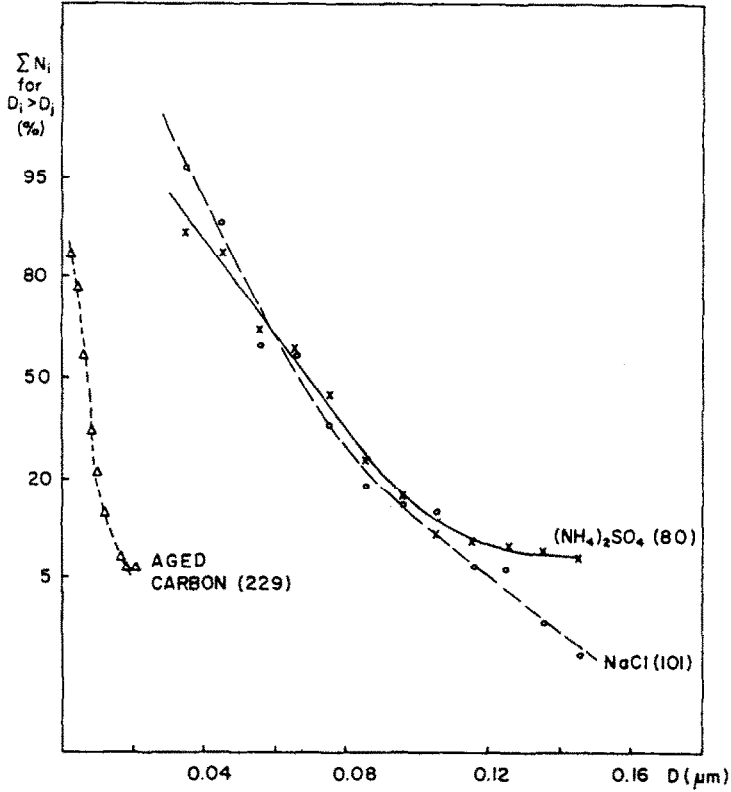


Fig. 4. Size distribution of test aerosols. Salt aerosol was prepared by dispersing and evaporating salt solution drops and storing the aerosol for 1.5 h. Carbon aerosol was stored for 24 h.

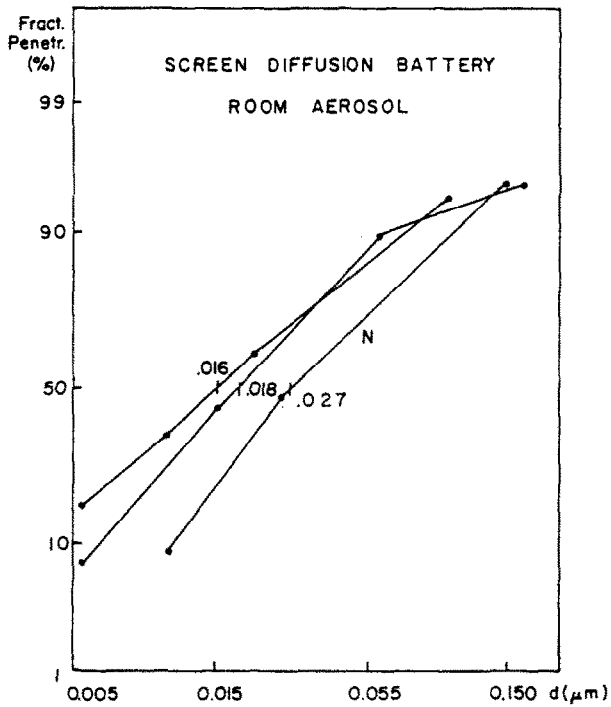


Fig. 5. Room aerosol size distribution with marked median particle diameters. N— aerosol passed through a Kr-85 neutralizer.

carbon or nichrome wire particles and also appropriate when salt aerosol was generated by a furnace technique. In the case of salt solution atomization, subsequent slow droplet drying and particle storage, the charge effect on particle deposition and coagulation was less pronounced.

RESULTS OF COUNTER COMPARISON

Because the N-P counter is often used as secondary calibration standard while it itself was calibrated by an Aitken type absolute counter, attention has mainly been paid to the comparison of N-P counter with the UMR-AAN counter. There was also an intention to compare these data with two other counters widely used in field experiments (GE automatic AN counter and GA manually operated counter) in a wide range of AN concentrations and for different kinds of aerosols. At the time of the main comparative measurements, N-P counter No. 922 was the only one available to the investigators. For this reason all AN concentrations measured by other counters are plotted against the percentage of the total transmission measured by the photocell of N-P counter No. 922. This counter was later compared with a N-P counter No. 920 which was originally compared with Prof. Pollak's counter in Ireland (Alle, 1968). This cross correlation of data was made with room air aerosol in the concentration range within 140 to 26 000 AN cm^{-3} . Most of the points showed that the deviation of both counters is not greater than 5% of the measured extinction and that

only in a few cases it surpasses 5% (in 3 out of 25 measurements). This enables one to correlate the data of a specific counter to the prototype N-P counter.

In Figure 6 are summarized data obtained by the UMR counter in comparison to the N-P No. 922 counter. The individual curves were obtained as the regression line of a parabola curve fitting of the data from measurements which are depicted in Fig. 7 for sodium chloride and, in Fig. 8, for carbon aerosol. Similar curves were plotted for $(\text{NH}_4)_2\text{SO}_4$, Ni-Cr and room aerosol. Each curve contains bars of uncertainty around each point indicating potential deviation of the measured value due to the expected mean errors of counting with the UMR counter. There is a large scatter of data which were sometimes taken during several days of measurement with the same, however, differently aged aerosol. Disregarding one data point in the case of sodium chloride aerosol, all of the plotted data support the idea that UMR-AAN counter, operated at a supersaturation of 2.5, counts higher than the prototype N-P counter No. 920 and the GE, GA and N-P counter No. 922 (Tables 2 and 3). The curves in Fig. 6 and individual points in figures similar to Figs 7 and 8 reveal that hygroscopic aerosols lead to only slightly higher counts in the UMR-AAN counter at the AN concentrations higher than 20,000 AN cm^{-3} , however, non-hygroscopic nuclei, such as carbon or Ni-Cr aerosol show considerably higher counts at concentrations surpassing 30,000 AN cm^{-3} . The explanation for this discrepancy of the measure-

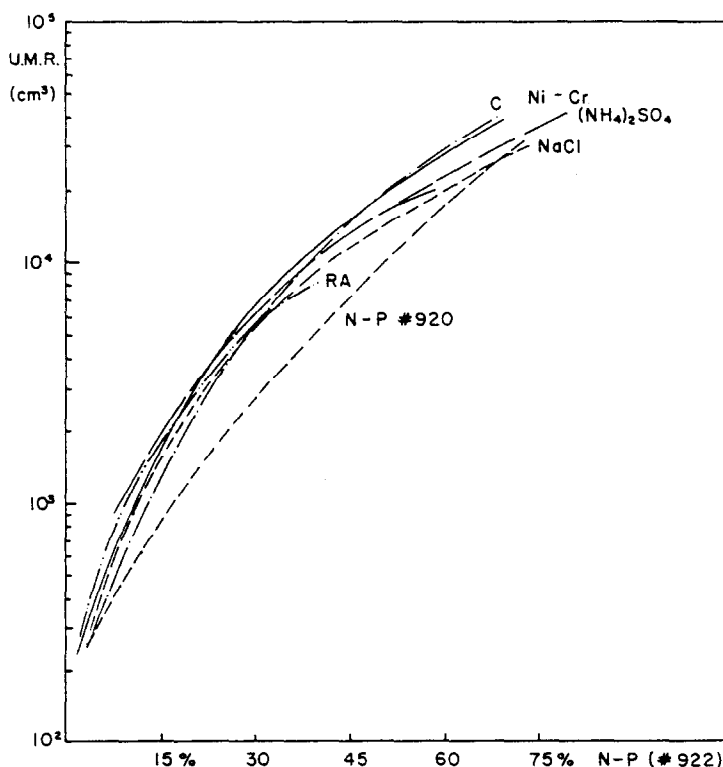


Fig. 6. Comparison of the UMR-AAN counter and two N-P counters for different test aerosol. RA—room air aerosol.

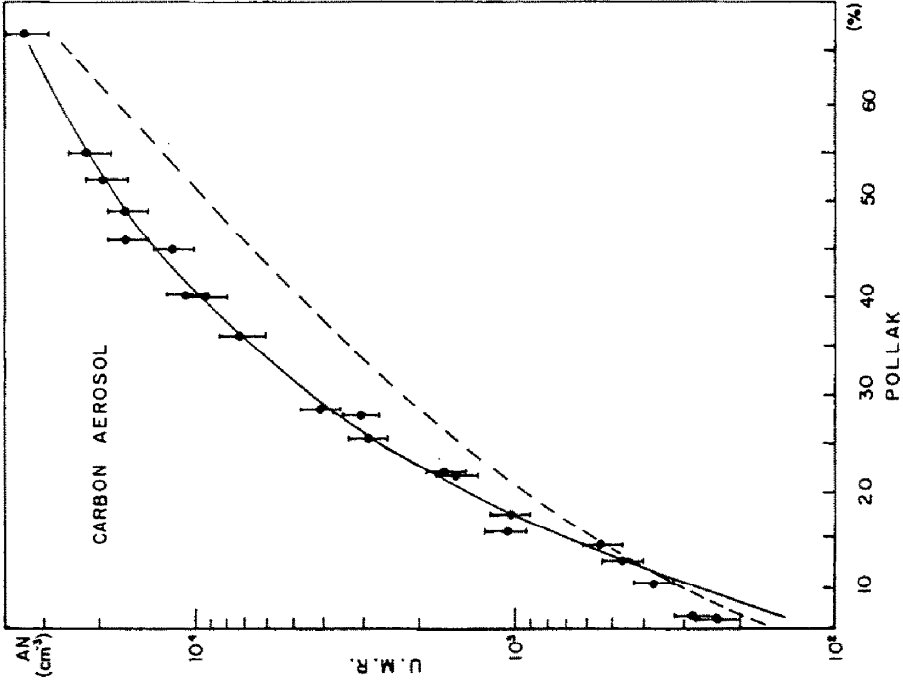


Fig. 8. N P Counter light extinction measurement vs UMR-AAN counter direct concentration measurement of carbon aerosols. Full line: N P No. 922. Dashed line: N P No. 920.

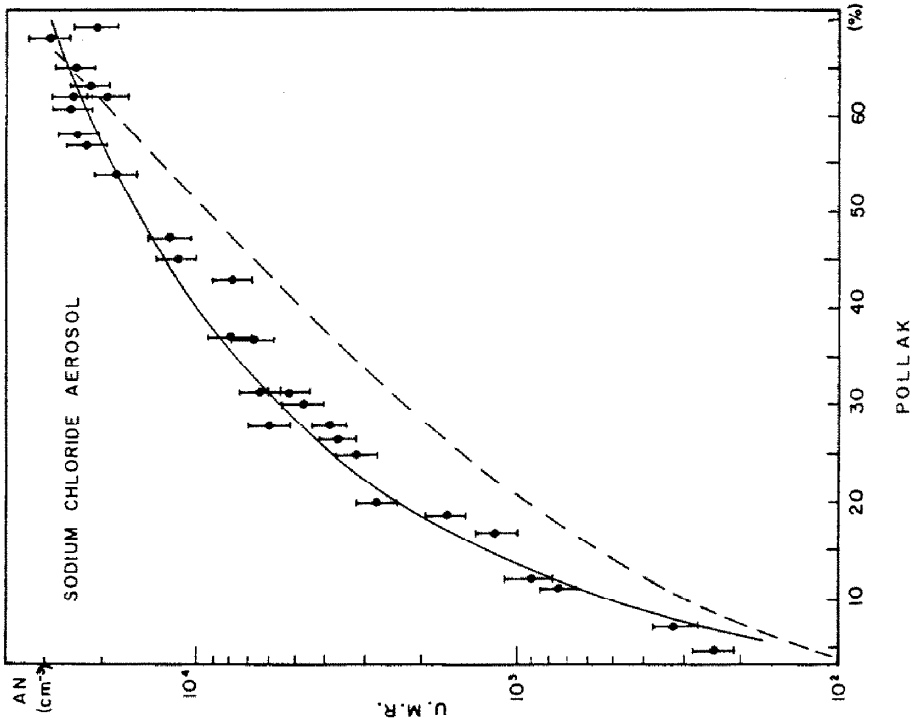


Fig. 7. N P Counter light extinction measurement vs UMR-AAN counter direct concentration measurement of sodium chloride aerosol. Full line: N P No. 922. Dashed line: N P No. 920.

ments at high AN counts can be found in the hypothesis that not all nuclei are activated due to the deficiency of available water vapor and due to the lower supersaturation achieved in the counters sensitive volume. Also, one cannot exclude the possibility of systematic deviations of both N-P counters while using room aerosol for comparison. This is apparent for plotting curves similar to Fig. 7 and 8 for GE and GA counters and comparing the data for hygroscopic and non-hygroscopic particles at high concentration (Podzimek *et al.*, 1980).

Tables 2 and 3 summarize the mean relative deviations $\left[\frac{N(\text{UMR}) - N(\text{GE})}{N(\text{UMR})} \right]$ of AN concentrations measured by GE and GA counters from the UMR-AAN counter for different aerosol and AN concentrations. It appears that with several exceptions, both counters which were originally calibrated against N-P counter measure lower concentrations than UMR-AAN counter with the GE counter approximately 37% and GA 23% for the average concentration range of 300 to 2.0×10^4 AN cm^{-3} and for the five different kinds of aerosol.

The results of AN comparison show that there are differences in AN counting by individual counters depending upon the concentration range of AN and probably upon the nature of nuclei. These differences are caused by different supersaturation and different geometry of an individual counter. In general they support the statement by Podzimek and Kassner

(1976) that the indirect comparison of data published by Cadle *et al.* (1975) would lead to the conclusion that the UMR-AAN counter measures approximately 30% higher in AN concentrations compared to counters used during the Boulder workshop. If one will reduce the problem to the comparison of a secondary standard, N-P counter, with an absolute counter, UMR-AAN counter, two main questions ought to be answered first: Are the concentration differences between an absolute and relative counter significant with regard to the error analysis in UMR-AAN counter? Are the higher counts of the UMR-AAN counter due to its higher supersaturation—which is contradictory to the often assumed plateau in nuclei counts vs expansion pressure ratio curve around pressure ratio of 1.21—or are they due to the basic difference in geometry and sensitive volume of the counters (Kassner *et al.*, 1968b).

Among several sources of potential errors in measuring AN concentration with UMR-AAN counter the human factor in counting the droplet images on a projection screen and inhomogeneities of droplet distribution in counters sensitive volume should be mentioned first. A more detailed analysis (Podzimek *et al.*, 1980) showed that the first factor might account for $\pm 1\%$ to $\pm 2\%$ if droplet concentrations in the projected space are larger than 100 cm^3 . The errors due to droplet inhomogeneity in the counters sensitive volume was estimated to be around 10% of the counted AN concentration if the nuclei concentration

Table 2. Mean relative deviation of AN concentrations measured by GE Counter from the UMR-ANN Counter

-AN(cm^{-3}) $\times 10^3$	Mean rel. dev. (%) for aerosol					
	NaCl	(NH_4) ₂ SO ₄	Ni-Cr	Carbon	Room air	Mean %
20	19	0	38	7		16.0
10	29	17	41	13	(39)	27.8
5	34	21	47	12	44	31.6
2	39	41	43	23	43	37.8
1	41	55	56	31	44	45.4
0.6	40	64	56	40	46	49.2
0.3	33	76	51	46	41	49.4
Mean	33.6	39.1	47.4	24.5	41.6	37.3

Table 3. Mean relative deviation of AN concentrations measured by GA Counter from the UMR-AAN

AN (cm^{-3}) $\times 10^3$	Mean rel. dev. (%) for aerosol					
	NaCl	(NH_4) ₂ SO ₄	Ni-Cr	Carbon	Room air	Mean %
20	9	-7	13	0		3.8
10	17	1	23	9	(16)	13.2
5	18	18	30	12	23	20.2
2	20	33	38	20	37	29.6
1	32	47	47	33	41	40.0
0.6	-3	54	54	26	35	33.2
0.3	-4.3	63	23	5	0	17.3
Mean	12.7	29.9	32.6	15.0	25.3	22.5

was kept between 100 and 300 cm⁻³. This optimal range of nuclei concentration can be easily adjusted in the UMR-AAN counter because of its inherent dilution effect during sampling, which itself, however, introduces an error. The magnitude of this error depends on the accuracy of pressure change measurement during sampling process. It is assumed that they cannot be greater than a few per cent (Podzimek *et al.*, 1980, p. 108).

The droplet coincidence 'losses' connected with the distortion of the photographic record due to the out-of-focus position of the droplets represents an important source of errors which, however, can be limited by using an appropriate dilution of the sample (Podzimek *et al.*, 1980, Appendix). If the droplet (AN) concentration in the sensitive volume will be between 100 and 300 cm⁻³ there is a good reason to expect that the total possible errors in AN counting in the UMR-AAN counter will not surpass 20% of the measured concentration. In conclusion, the higher counts of the UMR-AAN counter are real, reproducible and cannot be explained by the potential errors in AN counting either by N-P or UMR-AAN counter.

The second question can be answered by estimating the potential increase in AN counts if the expansion pressure ratio in N-P counter will be increased from the value of 1.21 (corresponding to N-P counter) to 1.33 used in the UMR-AAN counter. Similar study has been performed with room air and sodium chloride aerosol and is the subject of a special publication (Podzimek and Yue, 1981). Here only the main conclusions are reported: The room aerosol at the AN concentration of 1245 AN cm⁻³ yielded a 37% increase in AN counts if the expansion pressure ratio of 1.33 instead of 1.21 was used. At the concentration of 5624 AN cm⁻³ the measured increase in AN counts was 28%. A similar study performed with sodium chloride aerosol showed the increase of 18% for AN concentration of 2406 cm⁻³, 36% for 8785 AN cm⁻³ and 31% for 33,558 cm⁻³ if the expansion pressure ratio increased from 1.21 to 1.33. At higher AN concentrations the increase in counts due to the changing expansion pressure ratio might be even higher (e.g. 63% for 69,182 AN cm⁻³). This value, however, might be influenced by two factors, which can hardly be separated in case of counting AN at concentration higher than 35,000 cm⁻³ and referring all counts of the N-P counter to the AN concentration level measured by GE counter: the real AN concentration increases due to the higher supersaturation at the higher pressure expansion ratio and the 'artificial' increase of the value of the ratio $\frac{N(N-P)}{N(GE)}$ due to the lower AN counts by GE at very high nuclei concentration. There is a strong indication that at a concentration higher than 30,000 AN cm⁻³ not all nuclei will be activated during the fast cycling expansions in the GE counter.

In general, one concludes from the experiments with the influence of higher expansion pressure ratio in the N-P counter on the AN counts that the difference in

AN concentrations measured by the UMR-AAN counter and the N-P counter is mainly due to the higher supersaturation ratio used in the former counter. The AN concentration differences found by the direct counter comparison and by the increased pressure ratio in the N-P counter are close.

CONCLUSION

The analysis of different processes affecting the AN activation in the N-P counter reveals the complexity of problems related to the calibration of a specific AN counter and to the finding of an ideal standard for such a calibration.

On one hand, AN measuring techniques become more difficult and less reproducible with decreasing particle size and concentration. On the other hand, AN concentration measurements at concentrations higher than 50,000 cm⁻³ become inaccurate if one does not know the particle composition and the size distribution and if the counter calibration had not been done in conditions similar to the intended measurement. For instance, the comparatively short residence time of nuclei in the sensitive volume of GE counter (approximately 0.2 to 0.3 s) suggests that nucleated drops may lack sufficient growth time to achieve their 'equilibrium radius', especially at low nuclei concentration (Fig. 2). In this case an extinction measurement might depend considerably on the physico-chemical properties of nuclei (composition, condensation coefficient) besides on their number and size distribution. Figure 2 shows also that in a polydispersed aerosol at very high nuclei concentration, the smallest nuclei might not grow to a size effective in light extinction measurement. This will affect mainly automatic GE counter with fast cycling expansion.

UMR-AAN counter records larger AN counts than N-P counter and both of the other counters. These differences range between 20 and 40% of the measured nuclei concentration depending on the concentration and nature of the test aerosol. They are caused mainly by the higher supersaturation (2.5) used in the UMR-AAN counter. This fact opens an interesting discussion of how far AN counter can be considered as a total submicron particle counter and what supersaturation should be used related to water surface for its successful function. Another interesting subject—closely related to the investigation of the potential function of AN counter as a total particle counter—is the threshold (smallest) size of an activated nucleus in a specific counter which apparently depends also on the AN concentration and size distribution. It appears that expansion pressure ratio of 1.30 or 1.35 in the N-P counter would yield better results in counting almost all particles just before the condensation on light ions starts. Because UMR-AAN counter is not void of counting errors which might reach the value of 20% of the counted concentration (at very low or very high AN counts), one should not be surprised if the

current counters used in highly polluted environment of automotive transport would yield data which are 80% lower than reality. In order to justify this statement one would need, however, to design a special experiment, with well controlled AN concentrations higher than $100,000 \text{ cm}^{-3}$ which itself is a very difficult task.

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REFERENCES

- Allee P. (1968) Calibration of the Pollak photo-electric nucleus counter, *J. Rech. Atmos.* **III**, 97–99.
- Beard K. V. and Pruppacher H. R. (1971) A wind tunnel investigation of the rate of evaporation of small water drops falling at terminal velocity in air. *J. Atmos. Sci.* **28**, 1455–1464.
- Bricard J., Madeleine G., Reiss P. and Turpin P. V. (1972) Compteur de noyaux de condensation a flux continu. *C. R. Acad. Sc. Paris t.* **275**, 837–840.
- Burckhardt H. and Flohn H. (1939) *Die Atmosphärischen Kondensationskerne in Ihrer Physikalischen und Bioklimatologischen Bedeutung*. J. Springer, Berlin.
- Cadle R. D. (1975) *The Measurement of Airborne Particles*. J. Wiley & Sons, New York.
- Cadle R. D., Langer G., Haberl J. B., Hogan A., Rosen J. M., Sedlacek W. A. and Wegryzn J. (1975) A comparison of the Langer, Rosen, Nolan–Pollak and SANDS condensation nucleus counters. *J. appl. Met.* **14**, 1556.
- Carstens J. C. (1979) Drop growth in the atmosphere by condensation: Application to cloud physics. *Adv. Colloid Interface Sci.* **10**, 285–314.
- Gormley P. G. and Kennedy M. (1949) Diffusion from a stream flowing through a cylindrical tube. *Proc. Ry. Acad.* **52A**, 163.
- Grant O. (1970) *Report on Workshop Goals, Programs, Instruments, Observations, and Preliminary Analyses, 2nd. Inter. Workshop Condens. Ice Nuclei*, CSU, Fort Collins, 1–149.
- Jaenicke R. and Kanter H. J. (1976) Direct condensation nuclei counter with automatic photographic recording, and general problems of "absolute" counter. *J. appl. Met.* **15**, 620–632.
- Kanter H. and Junge C. E. (1971) A new automatic condensation nuclei counter for low particle concentrations, *Supl. Vol. Proc. 7th Int. Conf. Condens. and Ice Nuclei*, Prague and Vienna, Sept. 1969. Academia, Prague, 205–212.
- Kaselau K. H., Fabian P. and Rohrs H. (1974) Measurements of aerosol concentration up to a height of 27 Km. *Pageophys.* **112**, 877–885.
- Kassner J. L., Jr., Carstens J. C., Vietti M. A., Bierman A. H., Yue Paul C. P., Allen L. B., Eastburn M. R., Hoffman D. D., Noble H. A. and Packwood D. L. (1967) Expansion cloud chamber technique for absolute Aitken nuclei counting. *J. Rech. Atmos.* **III**, 45–51.
- Kassner J. L., Jr., Carstens J. C., and Allen L. B. (1967) The myth concerning the condensation nucleus counters, *Inter. Atmos. Nuclei Instrum. Workshop*, Lannemezan, Sept. 1967, 1–33; also *J. Rech Atmos.* **III**, 25–31 (1968a).
- Kassner J. L., Jr., Carstens J. C. and Allen L. B. (1968b) Analysis of the heat and vapor propagation from the walls of the Nolan, Pollak and Gardner type condensation nucleus counters. *J. Atmos. Sci.* **25**, 919–926.
- Landsberg H. (1938) Atmospheric condensation nuclei. *Gerl. Beitr. z. Geophysik Suppl. Band III. Ergeb. Kosm. Phys.* **3**, 155–252.
- Liu B. Y. H., Pui D. Y. H., Hogan A. W. and Rich T. A. (1975) Calibration of the Pollak counter with monodisperse aerosols, *J. appl. Met.* **14**, 46–51.
- Podzimek J. and Kassner J. L., Jr. (1976) Comments on comparisons of condensation nucleus counters. *J. appl. Met.* **15**, 1333–1336.
- Podzimek J., Carstens J. C. and Yue P. C. (1980) *The Measurement and Identification of Ultrafine Aerosols in Polluted Air*. Final Report DOT RC-82009, U.S. Department of Transportation, Washington, D.C., December 1979.
- Podzimek J. and Yue P. C. (1981) A note on the use of a photoelectric counter for total particle counting. *J. Aerosol. Sci.* (submitted)
- Pollak L. W. (1959) Counting of Aitken nuclei and applications of the counting results. *Air Pollut.* **1**, 293–306.
- Pollak L. W. and Metnieks A. L. (1957) The influence of scintillation on the measurement of extinction with the photo-electric nucleus counter at very low concentration. *Geofis. Pura e Appl.* **38**, 204–207.
- Pollak L. W. and Metnieks A. L. (1959) New calibration of photo-electric nucleus counter. *Geofis. Pura e Appl.* **43**, 285–301.
- Pollak L. W. and Metnieks A. L. (1960) The influence of pressure and temperature on the counting of condensation nuclei, Part I. Influence of pressure. *Geofis. Pura e Appl.* **47**, 123–141.
- Pollak L. W. and Metnieks A. L. (1961) The influence of pressure and temperature on the counting of condensation nuclei, Part II. Influence of low temperature. *Geofis. Pura e Appl.* **50**, 7–22.
- Preining O. et al. (1979) *Results of the WVFA-Workshop*, Vienna, May–June 1979. Institute Experim. Physics, Univ. Vienna, 1–47.
- Rosen J. M., Hofmann D. J. and Käselau K. H. (1978) Vertical profiles of condensation nuclei, *J. appl. Met.* **17**, 1737–1740.
- Rosen J. M., Hofmann D. J. and Laby J. (1974) *Stratospheric aerosol measurements II: The Worldwide Distribution*. Rept. HO, GM–22, Univ. of Wyoming, Laramie, August.
- Wagner P. (1974) *Untersuchung des Tröpfchenwachstums in einer schnellen Expansionsnebelkammer*. Ph.D. Dissertation, Universität Wien.
- Wegryzn J. E. and Podzimek J. (1975) *Calibration of the Stratospheric Aitken Nuclei Detection System (SANDS)*. Tech. Rep., GCCPR, University of Missouri-Rolla, March.