

An Improved Raindrop Chemistry Spectrometer

STUART G. BRADLEY,* STEPHEN J. ADAMS,* C. DAVID STOW* AND STEPHEN J. DE MORA†

*Department of Physics and †Department of Chemistry, University of Auckland, Auckland, New Zealand

(Manuscript received 20 July 1990, in final form 18 December 1990)

ABSTRACT

A spectrometer allowing size-fractional chemical analysis of raindrops has been described previously by the authors. Modifications to this raindrop chemistry spectrometer now allow improved performance in windy conditions. Instrument verifications show that drop-size distribution parameters can be estimated to 2%, and pH versus drop-size spectra can be obtained to 0.02 pH units in wind speeds up to 3 m s^{-1} . Improved resolution will allow trace chemical analysis for comparison with detailed rain chemistry models.

1. Introduction

Bradley (1985) described a "raindrop chemistry spectrometer" that sorts raindrops according to their size so that subsequent chemical analysis yields size-dependent chemical concentration spectra. First results from this instrument were given by Adams et al. (1986). Spectra of this kind are significant because they represent the only size-fractionated measurements available for comparison with chemical microphysical models of cloud and rain development in polluted environments.

Subsequent to the laboratory tests described by Bradley (1985), a number of further tests and important instrument modifications were made. It is the purpose of this paper to present the new information.

The principle of the spectrometer is as follows. Two flat spinning discs are driven by a common vertical shaft. The upper disc has a small radial slit, through which rain can enter into the space between the discs. Large drops, which have high fall speeds, meet the lower disc nearly beneath the slit (see Fig. 1). But small drops, which have low fall speeds, require sufficient time to cross the interdisc space that the lower disc has substantially spun by the time the drop meets it. Angular position at which a drop meets the lower disc is, therefore, a measure of drop fall speed and hence its size. By segmenting the lower disc with radial walls and collecting accumulated water into sample bottles at the periphery, a size spectrum is obtained, and chemical analysis as a function of drop size is possible.

Splashing is not a problem in this instrument since splashing does not occur at the high horizontal surface speeds of the discs. The main problems that arise involve compromising on the size of the slit, collecting

all the water, and handling errors due to drop horizontal velocity components in the presence of wind. If the slit is infinitely thin, each angular position around the lower (or *collector*) disc corresponds to just one drop size. As the slit is widened to allow more rain to enter, each angular position corresponds to a range of drop sizes, and obtaining a spectrum necessitates an inversion procedure. In practice, a design compromise can be reached, such that water collected in each segmented bin (or *sector*) is very closely identified with a single drop-size range. A slit (or *aperture*) of 20° width has been used in the instrument to date.

The remaining problems have been discussed by Bradley (1985) but will be discussed further here. We will also detail measurement procedures and uncertainties that were not discussed earlier.

2. Laboratory testing

A number of laboratory tests of spectrometer performance was conducted, in addition to those described by Bradley (1985).

a. Drop size

Filter paper dusted with rhodamine dye was taped into each sector on the collecting disc. Water drops were then allowed to fall 20 m, so as to reach terminal velocity before entering the spectrometer. The pattern obtained from a 60-s exposure to a random spray of drops is shown in Fig. 2. The larger stains are evident in sectors 1, 2, and 3 and the smallest in sector 7. The method of Cheng (1977) was used to estimate collected drop sizes from the dye stains. Results of a typical analysis are shown in Table 1. Drop-size ranges calculated using instrument geometry, rotation rate, and drop fall speed data agree closely with experimental values.

Corresponding author address: Dr. S. G. Bradley, Dept. of Physics, University of Auckland, Private Bag, Auckland, New Zealand.

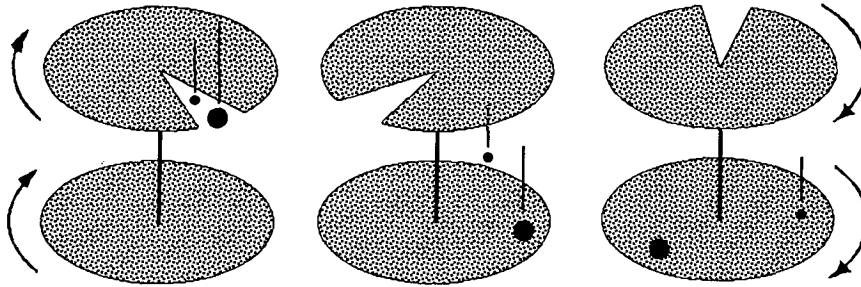


FIG. 1. The drop sorting and collection principle of the spectrometer.

b. Water collection

In order to check the possibility of handling procedures leading to a change in sample pH, water of known pH was poured into the spectrometer while it was running. The pH of the collected water was then compared with the original. After thorough washing of the collector disc, it is possible to reproduce pH to within ± 0.03 units.

Water losses were checked by pouring a measured weight of water into each sector and then running the spectrometer for a short time to simulate real use. Table 2 shows typical amounts of water lost due to incomplete drainage into the sample bottles. Visual observation of the collector disc after water has been drained reveals small droplets on the bottom of each sector, as well as small fillets of water at the boundaries. If it is assumed that p grams of water are retained along every meter of boundary and q grams become water beads on every

square meter of surface, then the total weight of water remaining in sector i is

$$L_i = b_i p + s_i q,$$

where b_i and s_i are, respectively, the boundary length and area of that sector. Solving the system of linear equations gives $p = 0.872 \text{ g m}^{-1}$ and $q = 12.2 \text{ g m}^{-2}$. Over the entire collector, nearly 4 g of water are lost to incomplete drainage at the boundaries and 2 g over the horizontal surfaces. For a rainfall rate of 10 mm h^{-1} , about 3 min would be required to collect this

TABLE 1. Drop radii typically found in each sector compared with radius ranges theoretically expected.

Sector	Stain diameter (mm)	Drop radius (mm)	Expected radius range (mm)
1	0.55	0.15	<0.24 and 1.07-2.00
	11.2	1.07	
	11.1	1.07	
	19.0	1.53	
2	8.9	0.93	0.85-1.36
3	6.4	0.74	0.70-1.01
	9.9	0.99	
	10.0	1.01	
	10.2	1.01	
4	4.7	0.61	0.58-0.81
	5.2	0.64	
	5.4	0.66	
	6.2	0.73	
	7.2	0.80	
5	3.2	0.47	0.46-0.65
	3.5	0.50	
	4.4	0.58	
	5.2	0.64	
6	2.0	0.34	0.30-0.49
	2.1	0.35	
	2.4	0.39	
	3.0	0.45	
	3.2	0.47	
	3.3	0.47	
7	1.0	0.23	0.24-0.30
	1.4	0.27	
	1.6	0.29	

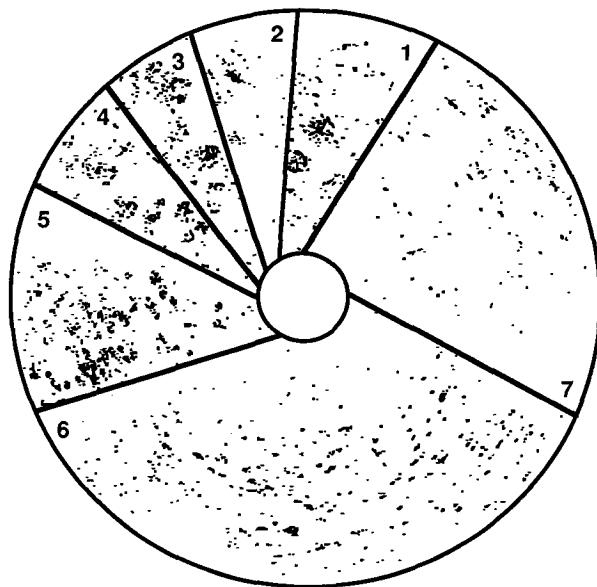


FIG. 2. A reduced copy of a filter paper placed inside the collector disc and exposed for 1 min to a spray of drops falling at terminal velocity.

TABLE 2. Two sets of results showing the amount of water lost from each sample due to poor drainage into the sample bottles.

Sector average (g)	Set 1			Set 2			Loss
	Weight in (g)	Weight out (g)	Weight lost (g)	Weight in (g)	Weight out (g)	Weight lost (g)	
1	2.10	1.48	0.62	4.20	3.60	0.60	0.61
2	1.40	0.87	0.53	2.80	2.29	0.51	0.52
3	1.40	0.88	0.52	2.80	2.27	0.53	0.53
4	1.70	1.13	0.57	3.40	2.82	0.58	0.58
5	3.10	2.35	0.75	6.20	5.43	0.77	0.76
6	9.40	7.83	1.57	18.80	17.28	1.52	1.55
7	5.90	4.78	1.12	11.80	10.66	1.14	1.13
Sums	25.00	19.32	5.68	50.00	44.35	5.65	5.68

much water; this represents an upper limit to spectrometer time resolution. Bradley (1985) soaked up the residual water with filter paper that was subsequently weighed. Negligible water losses were found, indicating that evaporation is not a major problem. For sequential sampling through a single rain event, it is desirable to dry the collector between samples so as to avoid cross contamination.

c. Interior airflow

Sarrazin and Zawadzki (1982) observed that the airflow within their spectrometer tended to cause drops to intersect the collecting disc at smaller angles than predicted. The effect was more marked for smaller drops, which have lower inertia and are exposed to the rotating air for a longer period. The result was reduced size discrimination. To investigate this problem, we used a small hot-wire anemometer to estimate speed

and direction of entrained air within the spectrometer. As shown in Fig. 3, airflow is strongest near the outside shield and spirals upward from the outside edge of the collector disc. As it approaches the upper disc, the air-stream is diverted toward the central axis, resulting in a more gentle downward flow near the axis. The effect of entrainment can be included in spectrometer evaluation by vector addition of the radially averaged air velocity (Fig. 4) to the external wind velocity. The results are a shift toward collection of smaller drops in each sector and a degradation of resolution in the narrow 2, 3, and 4 sectors. However, by placing a radial baffle across the space between aperture and collector discs, the internal circulation is impeded and becomes very much weaker, with the strongest flow vertical and near the baffle. Providing the baffle is sited beneath a masked-off region (see section 3), no drops will enter this region of disturbed airflow or splash off the baffle.

3. Reduction of wind speed dependence

After noticing degradation of spectrometer performance in the presence of wind, Sarrazin and Zawadzki (1982) installed their instrument at a sheltered site.

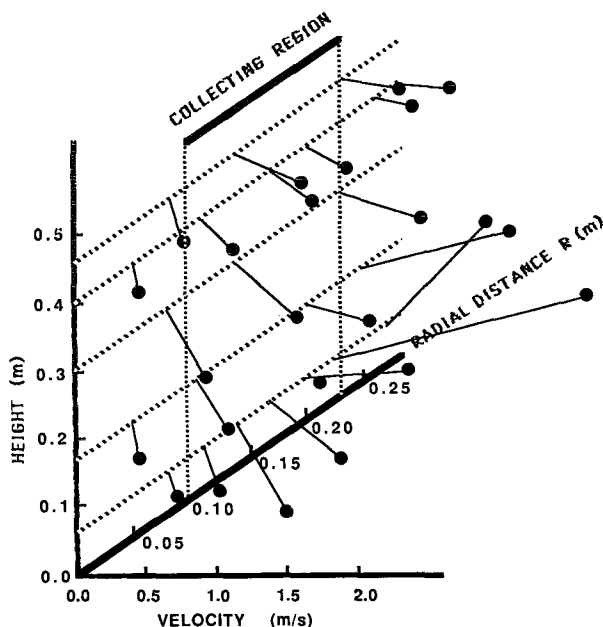


FIG. 3. Airflow measured within the spectrometer.

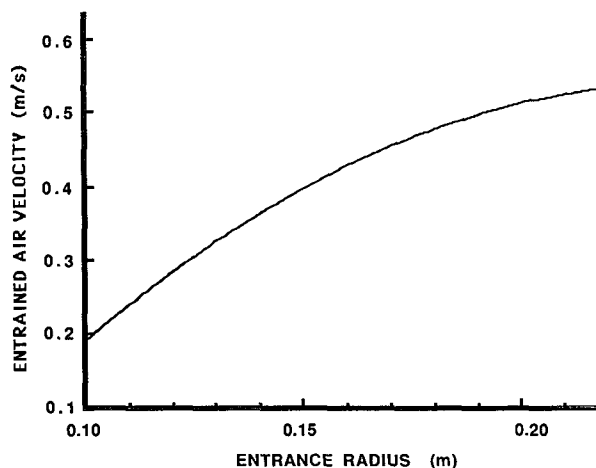


FIG. 4. The average entrained airspeed variation with radial distance *R* within the spectrometer.

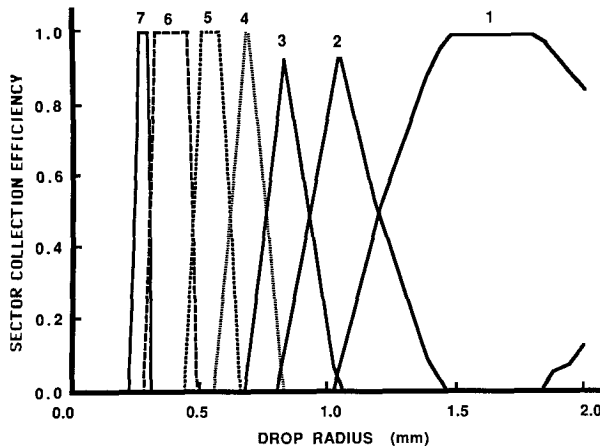


FIG. 5. The efficiency at which drops are collected by the seven collecting sectors.

However, calculations show that a sheltered fall of 10 m is necessary to reduce horizontal trajectory deflection to 1 cm m^{-1} for a 2-mm radius drop and 10 m s^{-1} wind. Turbulence within a sheltered structure of this size renders this approach impractical.

Bradley (1985) has explored wind-dependence of his spectrometer in some detail. As wind speed increases, the collection efficiency curves spread from the simple shapes shown in Fig. 5 into bimodal shapes, so as to decrease drop-size resolution. The collection efficiency modification may be understood as follows: as the entrance aperture moves upwind, drops entering the spectrometer will be moving horizontally in the opposite direction to the rotating collector disc. The drops will consequently be collected at larger collection angles, and each sector will contain drops of larger radii. Conversely, as the aperture moves downwind, the collector will be moving in the same direction as the horizontal motion of drops entering the spectrometer, and each section will contain smaller drops than it would

in still air. The combination of the two curve shifts produces a bimodal collection efficiency curve.

Two static masks have been designed to cover portions of the top of the spectrometer: the *radial mask* (Fig. 6a) allows only drops moving nearly radially to enter the spectrometer; the *tangential mask* (Fig. 6b) accepts mainly drops with a tangential velocity component, either in the sense of rotation (tangential mask A) or opposed (tangential mask B).

The radial mask has the effect of excluding drops that would be carried into the wrong sector by the wind. Cutouts of 90° , 45° , and 30° with wind speed 1 m s^{-1} were simulated. The samples in each sector become more independent as masking is increased (Fig. 7), but this is at the expense of reduced collection of rainwater. Figure 8 shows the fraction of drops that can land only in one sector. A mask with 45° cutouts gives nearly twice the resolution (as measured by the width of collection efficiency curves) of an unmasked spectrometer in a wind of 1 m s^{-1} .

The tangential masks exclude one of the bimodal peaks in the collection efficiency curves. Collection efficiencies for two semicircular configurations are shown in Fig. 9. There is a shift to collection of smaller drops when wind and rotation add, and a shift to collection of larger drops when wind and rotation oppose. The latter is preferable, however, because volumes collected should be closer to the zero-wind design. Also the size-resolution plots in Fig. 10 indicate greater independence of samples for tangential mask B.

The radial mask maintains the positions of the collection efficiency peaks near those of the still-air case; a knowledge of wind speed is not required in order to obtain a reasonable drop size or concentration spectrum. However, tangential mask B was selected for use with the spectrometer, since the time resolution is twice as good as that of the radial mask. The drop-size resolution is also better at higher wind speeds, providing the wind speed is known.

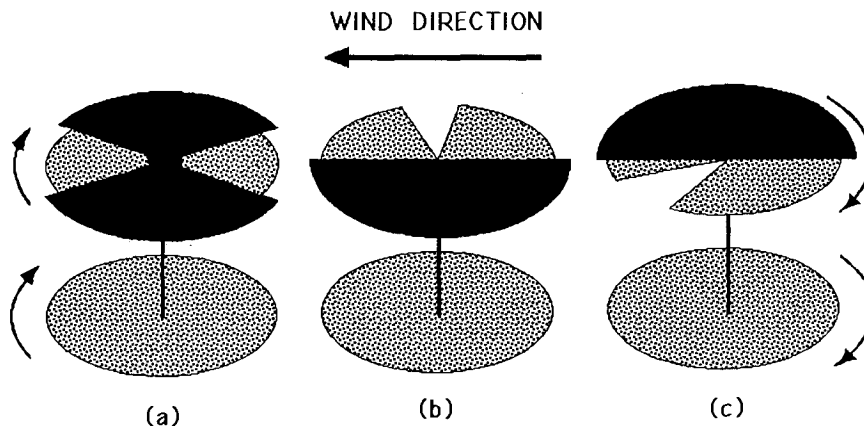


FIG. 6. The spectrometer with (a) radial mask, (b) tangential mask A, and (c) tangential mask B fitted.

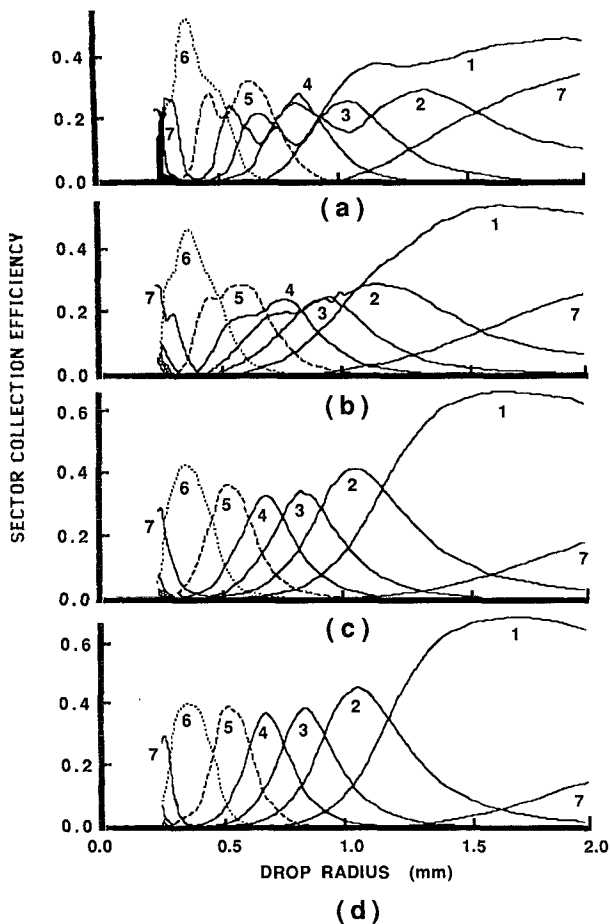


FIG. 7. Collection efficiencies for 1 m s^{-1} wind speed and radial mask cutouts of (a) 180° , (b) 90° , (c) 45° , and (d) 30° .

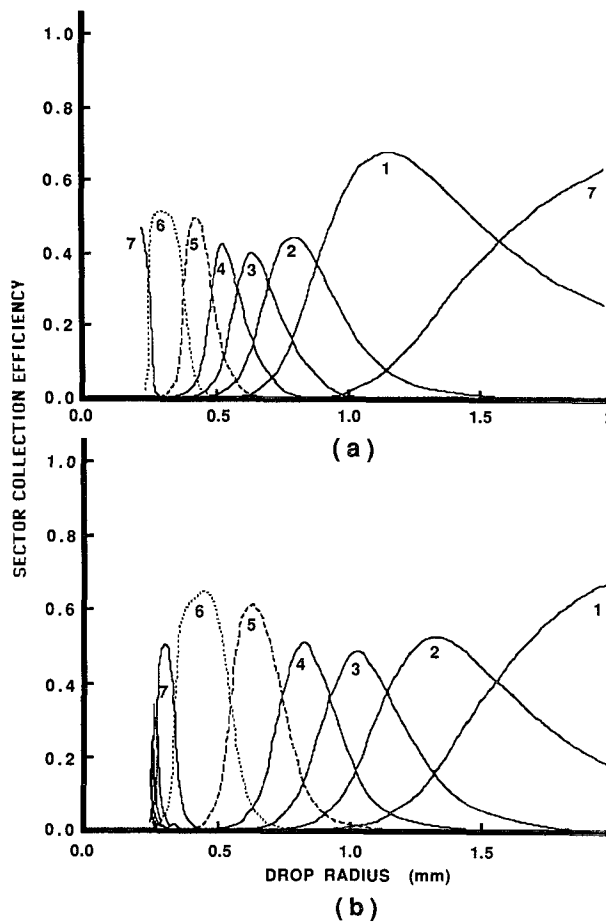


FIG. 9. Collection efficiency diagrams for tangential masks and 1 m s^{-1} wind speed: (a) wind and rotation add. (b) Wind and rotation oppose.

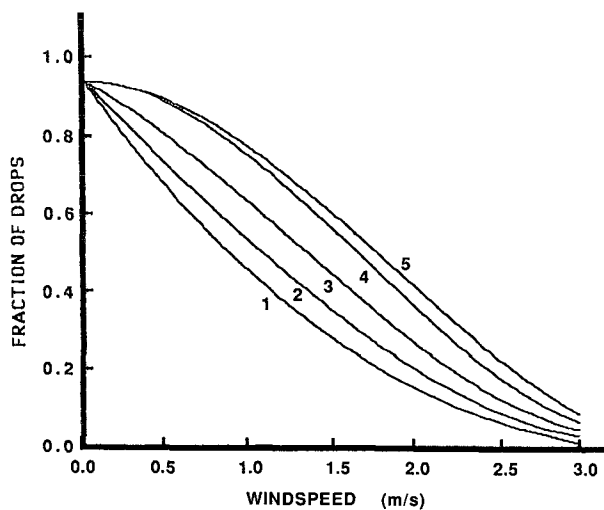


FIG. 8. Size resolution of the spectrometer plotted as a function of windspeed for radial mask cutouts of 1) 360° , 2) 135° , 3) 90° , 4) 45° , and 5) 30° .

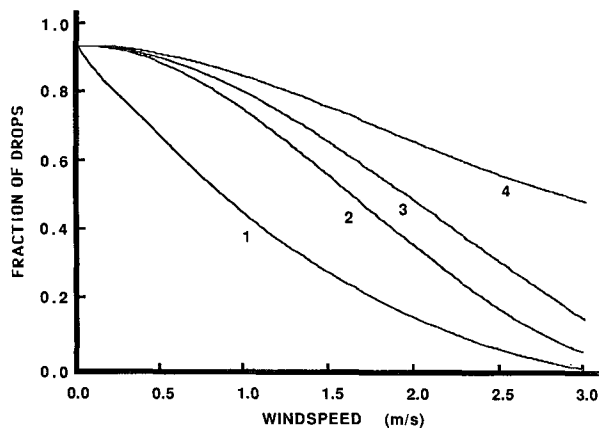


FIG. 10. Size resolution of the spectrometer plotted as a function of windspeed for masks of varying types: 1) no mask, 2) radial mask with 45° cutouts, 3) tangential mask A, and 4) tangential mask B.

A semicircular tangential mask B was constructed of 0.5-mm Lucite. Edges were raised and sharpened to reduce splashing into the spectrometer. The mask was attached to the spectrometer using a bearing at the top of the central shaft, and a small wind vane mounted on the mask allowed for self-alignment with wind direction. Wind tunnel testing showed that a threshold wind of $0.3 \pm 0.1 \text{ m s}^{-1}$ was required for alignment to occur. The mask aligned itself to within 5% of the wind direction with a response time of about 1 s for 0.5 m s^{-1} wind (the response should be faster with stronger winds). Simulations with 5° misalignment were negligibly different from correct alignment. The response time for drop trajectory changes is the terminal speed divided by gravitational acceleration, or about 0.1 s for 0.2-mm radius drops and 1 s for 2-mm drops (see Hosking et al. 1985; or Bradley 1985). The mask response is, therefore, reasonably matched to that of the larger drops that have collection efficiencies most affected by wind speed.

4. Measurement methods

The spectrometer was located at a very exposed urban site on the roof of a seven-floor building in Auckland, New Zealand. The aperture was sealed over between sampling events to prevent unwanted precipitation or dry fallout being collected. Whenever a suitable rain event appeared likely, both discs were rinsed thoroughly with deionized water, the wind vane and polythene collection bottles fitted, and the tape removed. If wind speed was consistently below 3 m s^{-1} and rain was imminent, the spectrometer was set in motion. The time was noted at the beginning and end of rainfall (or end of sampling). The spectrometer sectors were drained into the appropriate labeled bottles and rinsed with deionized water before another set of samples was collected. A bulk rain collector was positioned near the spectrometer, and wind speed and direction were monitored.

The volume of rainwater measured in the bulk collector was used to estimate average rainfall intensity over the sampling period. The formula of Marshall and Palmer (1948) could then be used to approximate the drop-size distribution sampled by the spectrometer. The volume of water collected in each spectrometer sample bottle was also recorded (by weighing) prior to chemical analysis and used to infer drop-size distribution.

A Schott N59 combination electrode connected to a Keithley 602 electrometer was used to measure pH in the rain samples. Standard American National Bureau of Standards (Weast 1982) buffer solutions were used for calibration purposes. The electrode system was therefore calibrated using solutions with ionic strengths near 10^{-1} M , whereas the ionic strength of rain water will usually be less than 10^{-3} M . Consequently, differ-

ent potentials would have developed across the ceramic junction in the pH electrode during calibration and measurement. The error introduced by assuming these potentials to be the same is typically less than 0.02 pH units (Stumm and Morgan 1970). Such a bias in pH measurements was considered acceptable, since our interest was in relative variations as a function of drop size. Stirring the samples during pH measurement could also have introduced streaming potential errors as large as 0.5 pH units. The samples were therefore thoroughly agitated and then allowed to come to rest before measurement. If the sample was larger than 2 ml, the sodium ion concentration was also determined. This involved aspirating the samples into an atomic absorbance spectrophotometer, then converting them into aerosol sprays that entered a high-temperature air-acetylene flame. The intensity of the 589-nm emission then gave sodium concentration. Five solutions containing sodium concentrations from 0 to $100 \mu\text{g ml}^{-1}$ were used for calibration. Potassium chloride was also

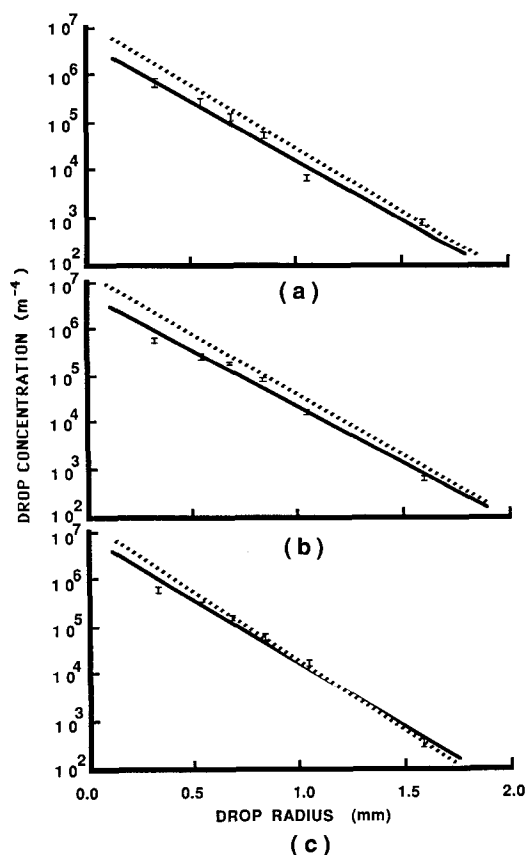


FIG. 11. Drop-size distributions. Dashed line: from a Marshall and Palmer (1948) distribution based on rainfall rates from bulk water collection. Solid line: best fit through the size distribution obtained from the spectrometer. Sample sets shown are (a) number 1, (b) number 3, and (c) number 4.

TABLE 3. Ancillary data for the eight datasets. (W = wind speed, R = rainfall rate, t = time after start of rainfall that collection began, duration = collection time, σ_{pH} = standard deviation of pH.)

Spectrum	W (m s^{-1})	R (mm h^{-1})	t (min)	Duration (min)	σ_{pH}	Bulk pH
1	2.9 ± 0.3	6 ± 0.5	0	40	0.39	5.26 ± 0.02
2	2.7 ± 0.3	4 ± 0.5	45	65	0.32	5.29 ± 0.02
3	0.5 ± 0.2	7 ± 0.5	30	30	0.07	5.54 ± 0.02
4	1.1 ± 0.2	4 ± 0.5	40	40	0.06	5.49 ± 0.02
5	0.7 ± 0.3	7 ± 0.5	0	22	0.29	5.30 ± 0.02
6	1.6 ± 0.3	5 ± 0.5	30	30	0.12	5.38 ± 0.02
7	1.9 ± 0.3	8 ± 0.5	0	24	0.43	5.29 ± 0.02
8	1.4 ± 0.2	5 ± 0.5	30	35	0.13	5.44 ± 0.02

present at 2000 ppm to suppress partial ionization of sodium (Thompson and Reynolds 1978).

5. Preliminary results

Eight complete datasets were obtained for natural rain. Figure 11 compares drop-size distributions estimated from rainfall rate (see Table 3) and the distributions derived from the sample volumes as described by Bradley (1985). The rainfall-rate method is expected to overestimate numbers of small drops (Willis 1984). For the three cases illustrated, the slopes derived from the lines of best fit through the spectrometer estimates differ from those calculated from rainfall rate by 1.4%, 4%, and 2%, respectively. The corresponding differ-

ences in rainfall rate are 7%, 20%, and 10%. Errors of this magnitude result in a 0.02 unit error in retrieved pH, and it would appear use of exponential drop-size distributions estimated from rainfall rate is a viable alternative to weighing samples.

Estimates of the pH distribution are shown in Fig. 12; these data have already been discussed by Adams et al. (1986). All results exhibit pH minima, suggesting that drops between 0.5- and 0.7-mm radius scavenge more efficiently. The observed shapes are similar to those predicted by Overton et al. (1979) for low NH_3 concentrations. The size of the most efficiently scavenging drops also agrees with that predicted by Graedel and Goldberg (1983) in some of their simulations.

6. Discussion

The tests and the results described previously and in Bradley (1985) and Adams et al. (1986) show that the raindrop chemistry spectrometer is a viable research tool. The addition of wind masks has extended its usefulness to environmental wind speeds of at least 3 m s^{-1} .

The results presented were all collected when the windspeed was less than 3 m s^{-1} . With the masks in place, drop sizes are well resolved at these speeds. Since we have taken great care, as described previously and in Bradley (1985), to identify and/or remove all foreseen sources of error, we believe the results to truly represent concentration spectra.

A number of mechanisms leading to a maximum $[\text{H}^+]$ in the vicinity of 0.6-mm drop radius has been proposed (Lopez-Valdivia 1987; Turner 1955). To identify the specific mechanism, further modeling work and sampling is required.

It is of interest that the drop-size spectrum obtained matched the Marshall and Palmer (1948) spectrum so closely. This suggests that, in the future, only chemical analysis need be performed, with spectrometer catch being predicted on the basis of rainfall intensity recorded by a conventional gauge and removing the requirement of careful weighing of bottles and samples.

The air masses studied have been clean air flowing

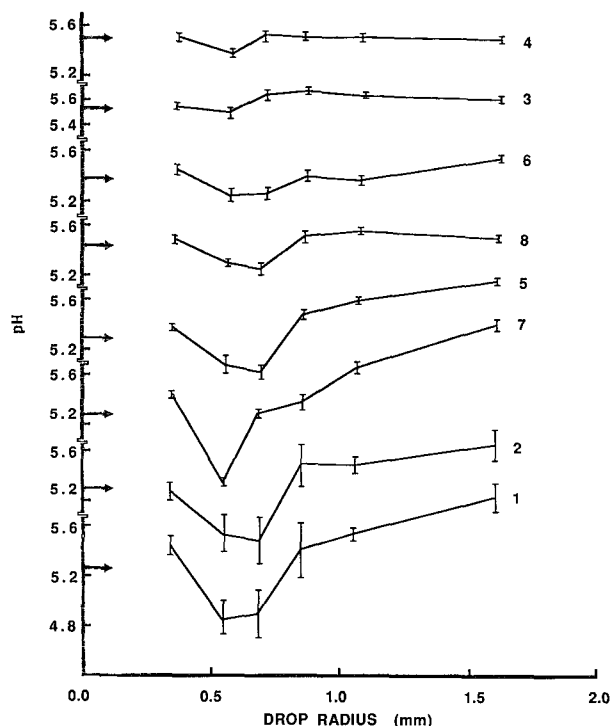


FIG. 12. Variation of pH with drop radius.

northeast from the Antarctic. It is important that the spectrometer be used in the future to study more common Northern Hemisphere continental and urban air masses.

Acknowledgments. The authors wish to express their appreciation to the referees for their constructive criticism.

REFERENCES

- Adams, S. J., S. G. Bradley, C. D. Stow and S. J. de Mora, 1986: Measurement of pH versus drop size in natural rain. *Nature*, **321**, 842–844.
- Bradley, S. G., 1985: A raindrop velocity spectrometer for drop chemistry investigations. *J. Atmos. Oceanic Technol.*, **2**, 190–200.
- Cheng, L., 1977: A stain method for measurement of drop size. *Environ. Sci. Technol.*, **11**, 192–194.
- Graedel, T. E., and K. I. Goldberg, 1983: Kinetic studies of raindrop chemistry. 1: Inorganic and organic processes. *J. Geophys. Res.*, **88**, 10 865–10 882.
- Hosking, J. G., C. D. Stow and S. G. Bradley, 1985: Corrections for horizontal winds and wind shear in raindrop size spectrometers. *J. Atmos. Oceanic Technol.*, **2**, 181–189.
- Lopez-Valdivia, S., 1987: A theoretical model of the washout of trace gases by raindrops in the atmosphere. Ph.D. dissertation, University of California, Los Angeles, 310 pp.
- Marshall, J. S., and W. M. Palmer, 1948: The distribution of raindrops with size. *J. Meteor.*, **5**, 165–166.
- Overton, J. H., V. P. Aneja and J. L. Durham, 1979: Production of sulfate in rain and raindrops in polluted atmospheres. *Atmos. Environ.*, **13**, 355–367.
- Sarrazin, R., and I. Zawadzki, 1982: A raindrop spectrometer for chemical analysis of precipitation (in French). *Atmosphere: Atmos. Ocean*, **20**, 39–49.
- Stumm, W., and J. Morgan, 1970: *Aquatic Chemistry*. Wiley Interscience, 583 pp.
- Thompson, K. C., and R. J. Reynolds, 1978: *Atomic Absorbance, Fluorescence, and Flame Emission Spectroscopy: A Practical Approach*. Wiley, 319 pp.
- Turner, J. S., 1955: The salinity of rainfall as a function of drop size. *Quart. J. Roy. Meteor. Soc.*, **81**, 418–429.
- Weast, R. C., 1982: *Handbook of Chemistry and Physics*, 63rd ed., Chemical Rubber Company, D–147.
- Willis, P. T., 1984: Functional fits to some observed drop-size distributions and parameterization of rain. *J. Atmos. Sci.*, **41**, 1648–1661.