

Note

Preliminary measurements of raindrop chemistry using an improved raindrop chemistry spectrometer

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Abstract Preliminary measurements of size-fractionated raindrop chemistry are described. These data were obtained with a modified version of the spectrometer described by Bradley in 1985 which allows improved performance in windy conditions. Mechanisms are discussed to account for observed concentration extrema at 0.6 mm drop radius. These extremes decrease with time from rain onset with a time constant of about 25 minutes.

Keywords rain chemistry; drop size distribution; rain spectrometer; acid rain; size-fractionated rain chemistry

INTRODUCTION

Bradley (1985) described a raindrop chemistry spectrometer which 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. Only a subset of the data now available was described in the Adams et al. (1986) letter. It is the purpose of the present paper to present this 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 (Fig. 1). But small drops, which have low fall speeds, require sufficient time to cross the inter-disc space so that the lower disc has spun substantially 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 because splashing does not occur at the high horizontal surface speeds of the discs. The main problems which do 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 as shown in Fig. 2. A slit (or "aperture") of 20° width has been used in the instrument to date.

The remaining problems have been discussed by Bradley (1985). Measurement uncertainties which were not discussed earlier are treated in Bradley et al. (1991).

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 with tape between sampling events to prevent unwanted precipitation or dry fallout being collected. Whenever a suitable rain event appeared likely, the collector disc was rinsed thoroughly with deionised water, polythene collection bottles fitted, and the tape removed. If wind speed was consistently below 3 m and rain 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 labelled bottles and rinsed with deionised 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 & 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.

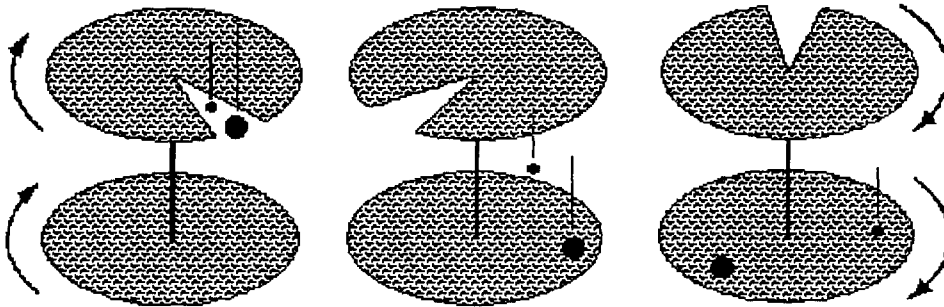


Fig. 1 The drop-sorting and collection principle of the spectrometer.

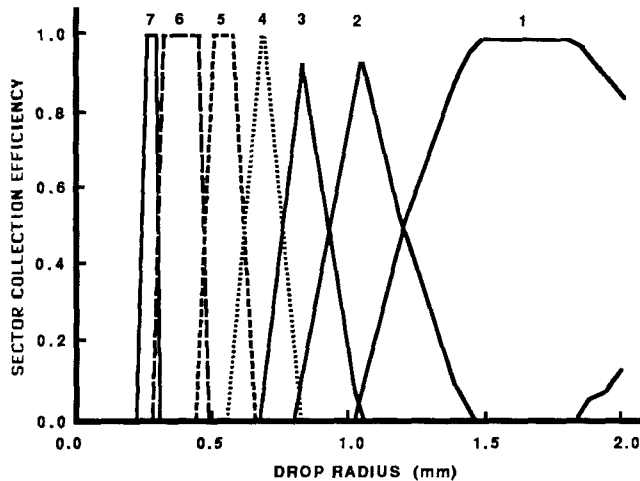


Fig. 2 The efficiency at which drops are collected by the seven collecting sectors.

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} mol, whereas the ionic strength of rainwater will usually be $<10^{-3}$ mol. Consequently, different 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 <0.02 pH units (Stumm & 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 which 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 $\mu\text{g/ml}$ were used for calibration. Potassium chloride was also present at 2000 ppm to suppress partial ionisation of sodium (Thompson & Reynolds 1978).

EXPERIMENTAL RESULTS

Eight complete data sets were obtained for natural rain embedded in clean air flowing northeast from the Antarctic. Figure 3 compares drop-size distributions estimated from rainfall rate (Table 1) 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 sample sets 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 differences 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 that 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. 4; 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)

Table 1 Ancillary data for the eight data sets. (*W*, windspeed; *R*, rainfall rate; *t*, time after start of rainfall that collection began; duration, collection time; σpH , spectrum variation.)

Spectrum	<i>W</i> (m/s)	<i>R</i> (mm/h)	<i>t</i> (min)	Duration (min)	σpH	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

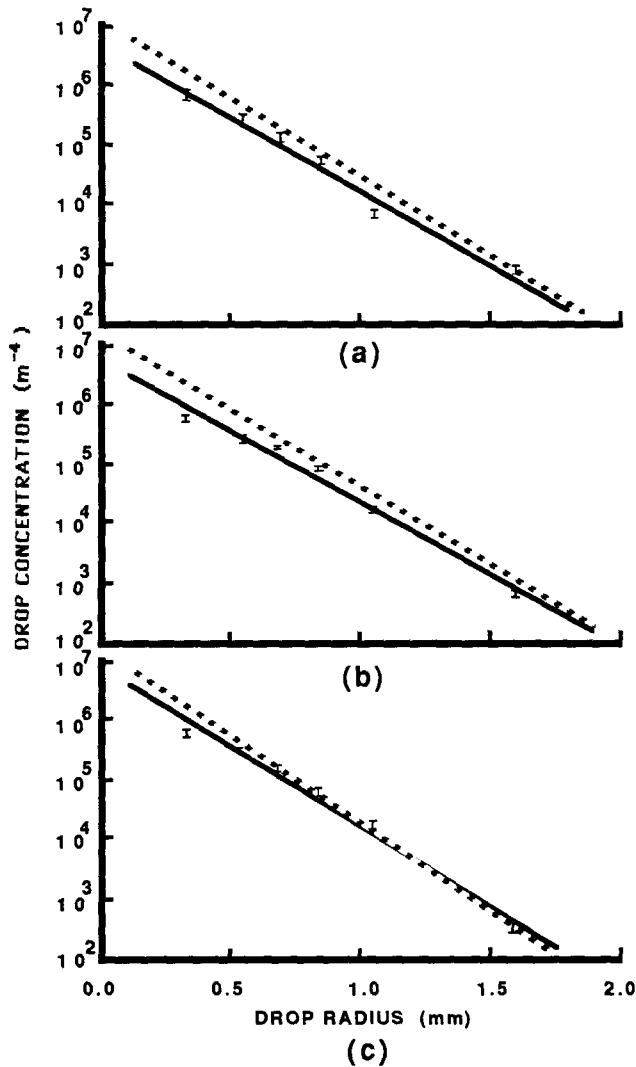


Fig. 3 Drop-size distributions. Dashed line: from a Marshall & Palmer (1948) distribution based on rainfall rates from bulk water collection. Solid line: best fit through the size distribution obtained from the spectrometer. Sample sets shown are (a) number 1, (b) number 3, and (c) number 4.

for low NH_3 concentrations. The size of the most efficiently scavenging drops also agrees with that predicted by Graedel & Goldberg (1983) in some of their simulations.

There are two likely explanations for the pH dependence on drop size. The first is that smaller drops are more efficient scavengers, both because the gas-to-aqueous transfer rate varies approximately as r^{-2} and because smaller drops have longer residence times. However, the higher concentrations are not seen in the smaller drops because they evaporate, coalesce with larger drops, or are produced by collisional breakup of larger, more dilute drops. The second mechanism is for rain to enter a relatively clean layer near the ground and for the smaller drops (having larger surface-to-volume ratio and slower fall speed) to desorb some scavenged species. This mechanism has been studied by Lopez-Valdivia (1987) in relation to the pH distributions shown in Fig. 4. For the cases discussed here, the latter mechanism is unlikely. The original air mass should be very clean, and the highest concentration of

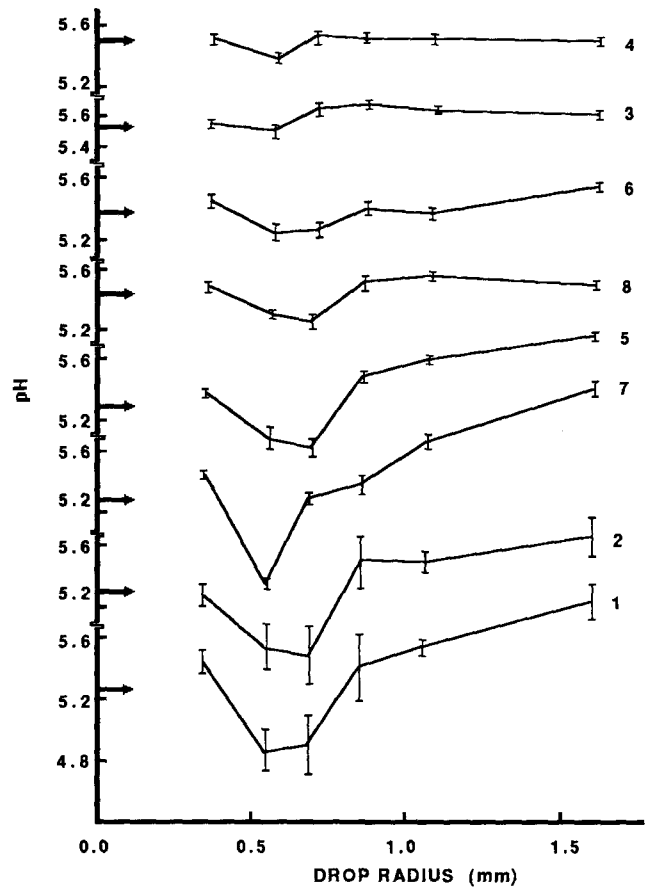


Fig. 4 Distributions of pH with drop radius. Data sets are identified by numbers at their right and are plotted in individual pH axes for clarity.

pollutants will be near the ground, because substantial mixing to greater heights is precluded by the short travel over the land.

As a measure of variation of pH with size, we have calculated the standard deviation σ_{pH} for each curve. This measure is shown plotted in Fig. 5 for sample duration as a function of time from onset of rain. Apart from observation set 2, there is clearly a tendency for σ_{pH} to decrease as the rain event progresses, and this is accompanied by an increase in bulk pH (shown by arrows on the left in Fig. 4). The time constant for flushing of the atmosphere can be crudely estimated from Fig. 5 as 25 min (if set 2 is ignored).

In order to obtain stable readings for sodium content, about 2 ml from each sector were required. As a consequence, only data sets 7 and 8 were suitable for analysis. The inversion method described by Bradley (1985) was used by defining $\text{pNa} = -\log_{10} [\text{Na}^+]$ and substituting pNa and $[\text{Na}^+]$ (in mol) for pH and $[\text{H}^+]$, respectively. Figure 6 illustrates the resulting variation of $[\text{Na}^+]$ with drop size. Set 7 contains both higher $[\text{H}^+]$ and $[\text{Na}^+]$. Minima occur at similar radii to that of the maxima of $[\text{H}^+]$.

Although only two $[\text{Na}^+]$ spectra are shown, they are consistent with each other. Spectra obtained by Komabayasi & Gonda (1964) and Turner (1955) show $[\text{Na}^+]$ minima at smaller radii near 0.4 mm, but this is possibly because these authors did not attempt to perform inversions of the type discussed by Bradley (1985).

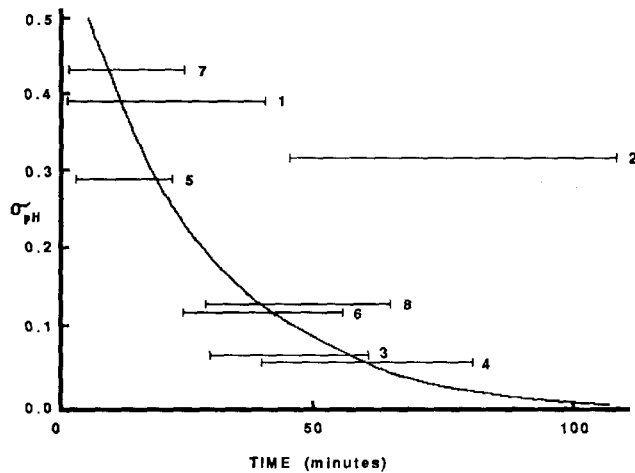


Fig. 5 The standard deviation of each set of pH measurements plotted against time from outset of rainfall. The duration of each sampling event is shown. The smooth curve is $0.6e^{-t/\tau}$ with $\tau = 25$ min.

Turner (1955) suggested a mechanism which is still considered viable: if cloud droplets form on sea-salt nuclei, then the largest drops will form on giant nuclei and grow faster by collection of smaller drops. Ultimately, the larger raindrops will, on average, contain higher chloride concentrations. Again, drop breakup will reflect large drop concentrations in small drop concentrations.

DISCUSSION

The results described above 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 as described in Bradley et al. (1991) has extended its usefulness to higher environmental wind speeds.

The results presented were all collected when the wind-speed was < 3 m; with the masks in place, drop sizes are well resolved at these speeds. Since we have taken great care, as described in Bradley (1985), to identify and/or remove all sources of error, we believe the results to truly represent concentration spectra.

A number of mechanisms leading to a maximum $[H^+]$ and a minimum $[Na^+]$ at 0.6 mm drop radius have been proposed. To positively identify the specific mechanism, further modelling work and sampling would be required.

The drop-size spectrum obtained matched the Marshall & Palmer (1948) spectrum 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 airmasses studied have been clean air flowing northeast from the Antarctic.

It is important that the spectrometer be used in the future to study more common Northern Hemisphere continental and urban airmasses.

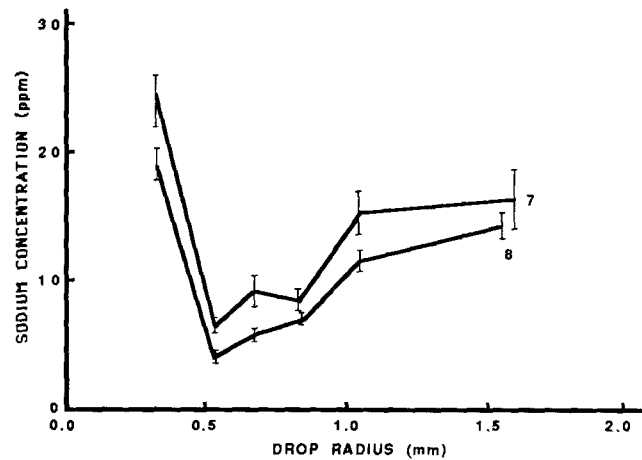


Fig. 6 Estimates of the variation in sodium content with drop size in natural rain. The numbers refer to the data sets from which the results were derived.

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