"Almost too sensitive," a new instrument can give particle size distribution and total particulate concentration of aerosols in air with short sampling time

cascade particle analyzer

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THE ATMOSPHERE contains an abundance of airborne particulate matter. Arising both from natural sources and the activities of civilization, these aerosols consist of solid particles and dispersed liquid droplets. Because of the diverse nature and origins of aerosols, conducting definitive studies is very difficult. In urban areas a measure of the total quantity present during a 24 hr period is obtained routinely using high volume filtration apparatus (1). Other monitoring devices using impaction-type nozzles and collection plates can segregate and measure aerosols according to size (2,3). Samples from these collection devices can be used for further analysis of inorganic and organic content.

A rapid particle analyzer

The P/Z Cascade Particle Analyzer (California Measurements, Sierra Madre, CA) now is providing some unique information about aerosols. A complete analysis of aerosol mass concentration and size distribution can be obtained from a sample of air taken for just several minutes. Collected samples of the sized particles are retained undisturbed and can be used directly to obtain composition, shape, and size information using auxiliary scanning electron microscopy (SEM) and x-ray fluorescence (XRF) techniques.

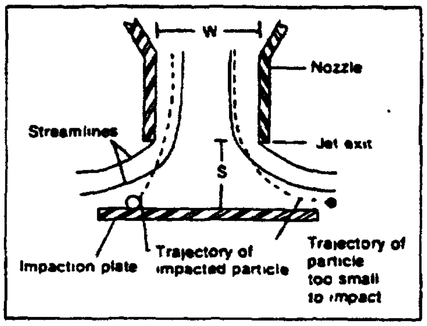
The instrument separates aerosol particles into 10 sizes from 0.05 to 25 μm. It does this by drawing the aerosol-laden air sample thru a series of 10 stages, each stage containing an inertial impactor jet of decreasing size. Directly below each jet is a piezoelectric quartz crystal coated with a thin adhesive film of "Apiezon-L" that is used as an impactor to collect the separated particles. As the jet of air exits from the nozzle it is forced to turn sharply to flow around the crystal. Larger particles in the stream, because of their inertia, continue to travel toward the crystal and impact on it. Smaller particles follow the flow of air around the crystal to the next stage, which is a repeat of the preceeding stage, except it is equipped with a smaller nozzle designed to impact smaller particles. The 10 stages thus collect

particles of smaller and smaller sizes.

Each crystal is the frequency-controlling element of a quartz-crystal microbalance (QCM), whose output frequency decreases when particles are collected on the surface. Placed in close proximity to the sensing crystal, but shielded from receiving impacted particles, is an identical reference crystal controlling the frequency of another circuit set about 2 kHz higher than that of the sensing crystal. The set of crystals in a stage are closely matched in frequency and have an AT cut to reduce drift with changes in temperature.

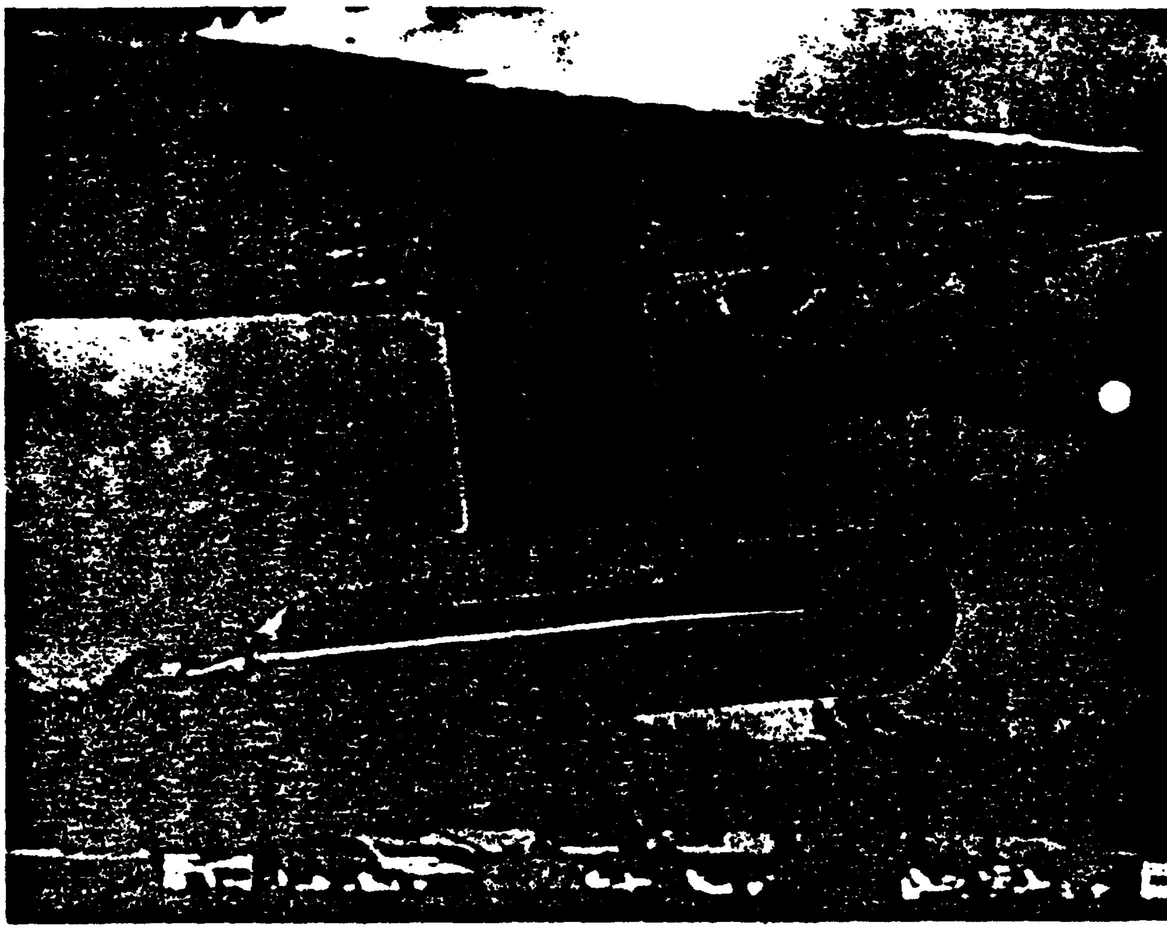
The beat frequency between the two oscillators is the signal indicative of the mass collected. A particle size distribution is obtained by monitoring the frequency change of the QCM in each of the 10 stages. This is done manually. After clean, filtered air is drawn thru the system, the initial frequency of each stage is printed out sequentially on a built-in printer. The aerosol sample then is drawn into the system for a predetermined time (30 sec for a 100 $\mu g/m^3$ concentration), and the changed frequencies are printed out. A simple calculation involving the change in frequencies over the time period and a stage constant will give the particle size distribution directly in $\mu g/m^3$. This calculation is done with a programable desk calculator-printer.

Sensitivity of the QCM is high. The essential electronics consisting of two oscillators and a mixer are built into a hybrid chip directly into each stage. Operating at 10 MHz, this arrangement of electronics and crystals gives a stability of 0.08 Hz/min., and a sensitivity of 10^9 Hz/g. This makes it pos-



Inertial impaction nozzles and collection plates separate and collect different particle sizes. Distances S, W and flow velocity are important variables

Airborne version (below) of analyzer was mounted in pod with isokinetic inlet under wing of NCAR aircraft for volcano plume sam--ing in background of pict. at Guatemala City airp..., during February 1978, is one of volcanoes.



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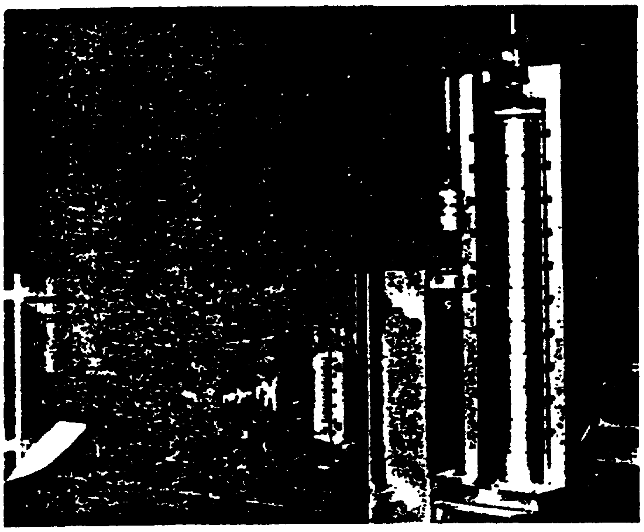
BATCo document for Province of British Columbia 12 April 1999 sible to detect 10^{-11}g quantities. At an air flow of 100 ml/min., a sampling time of 2 to 6 min. is adequate for analyses of aerosol concentrations ranging from 25 to 200 $\mu g/m^3$.

The instrument is almost too sensitive. At a particle loading equivalent to a frequency shift of about 400 Hz, the response becomes nonlinear. The crystal reaches a saturation limit near 2kHz shift (~6 μg added mass) and ceases to oscillate because of damping. For high concentration samples, the sampling period must be restricted to less than 30 sec to avoid saturation.

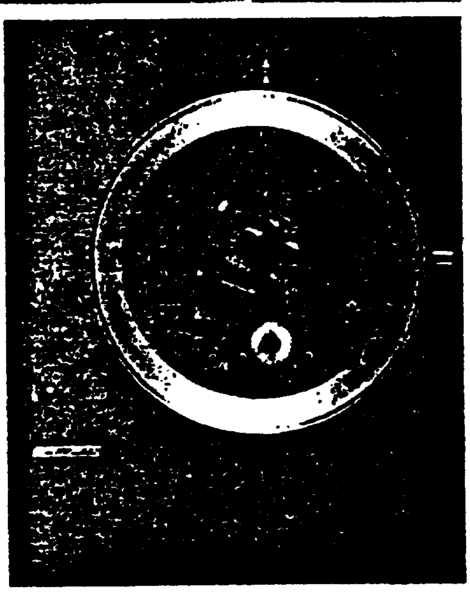
A loaded crystal can be turned over and the other side used for sensing. It can be removed for further analysis of the deposit, or cleaned by washing with a small amount of hexane.

Applications are unique

The instrumental components are rugged enough to be mounted inside aircraft or in a pod under the wing for conducting survey studies. A number of unusual studies have been made (4).



P/Z Cascade Particle Analyzer *has 10-stage particle collectors assembled at right with valve at top of column to switch from completely filtered air used to establish zero reference, to direct sampling of aerosol-laden air. Frequency data from each stage can be observed on digital display and printed on printer. Jacks on panel are used with display when applying adhesive coating to crystals*



Removable cascade stage *has crystal in place above impaction nozzle to next stage. Hybrid chip electronics are mounted adjacent. At left, sensing crystal has been removed from three pins that mount it in exact position*

A vertical profile of aerosol size distribution over the Los Angeles Basin taken from a light plane showed the well-defined bimodal aerosol size distribution shifting as expected to greater fractions of submicron particles at the higher altitudes. Another study made from an automobile along a freeway extending over three counties showed the particle size distribution of smoke aerosols from a brush fire in the San Gabriel mountains. Aerial measurements of particulate size distribution from the plume of the Four Corners Power Plant showed a high concentration of 2.2 μm particles directly over the power plant. This study was able to show that 25 miles downwind, submicron ammonium sulfate particles had been formed at the expense of the SO_2 in the plume, which was converted at a rate of a few percent/hr.

Most of the aerosols in the upper atmosphere between 13 and 22 km are thought to come from volcanic eruptions. The spread of aerosols thruout the atmosphere from an eruption occurs over 1 to 2 yr. The P/Z Cascade Particle Analyzer is well suited to study the dispersion of these particles and the depletion mechanisms leading to their disappearance.

During February and March of 1978, a group of scientists in a specially instrumented aircraft flew 11 sampling missions over the active volcanoes of Pacaya, Fuego, and Santiaguito in Guatemala (5). Samples taken with the P/Z Cascade instrument were collected from inside eruption clouds and provide a detailed description of the distribution and nature of particles smaller than 25 μm.

For the Santiaguito volcano, the particle size distribution plot shows a peak at 0.4 μm. By removing the quartz-crystal collectors and using SEM and XRF techniques, the exact nature of the particles was determined. The particles larger than 1 μm were glassy agglomerates of minerals. The particles below 1 μm were aerosols of sulfuric acid droplets or very small crystalline compounds coated with sulfuric acid.

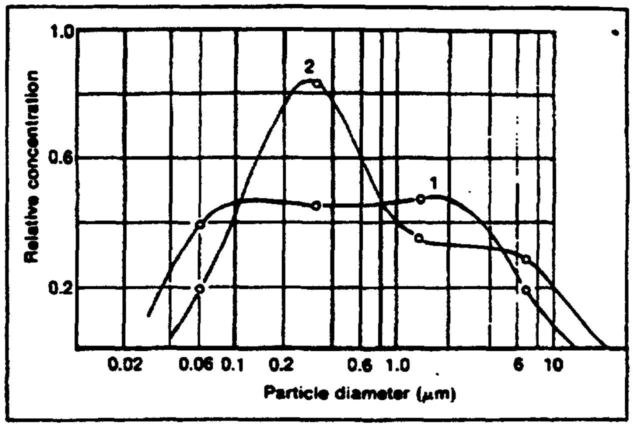
Analysis of air

Direct analysis of atmospheric air in urban areas of Los Angeles gives aerosol concentrations that vary from 30 to 500 $\mu g/m^3$ and particle size distributions that vary considerably with smog conditions.

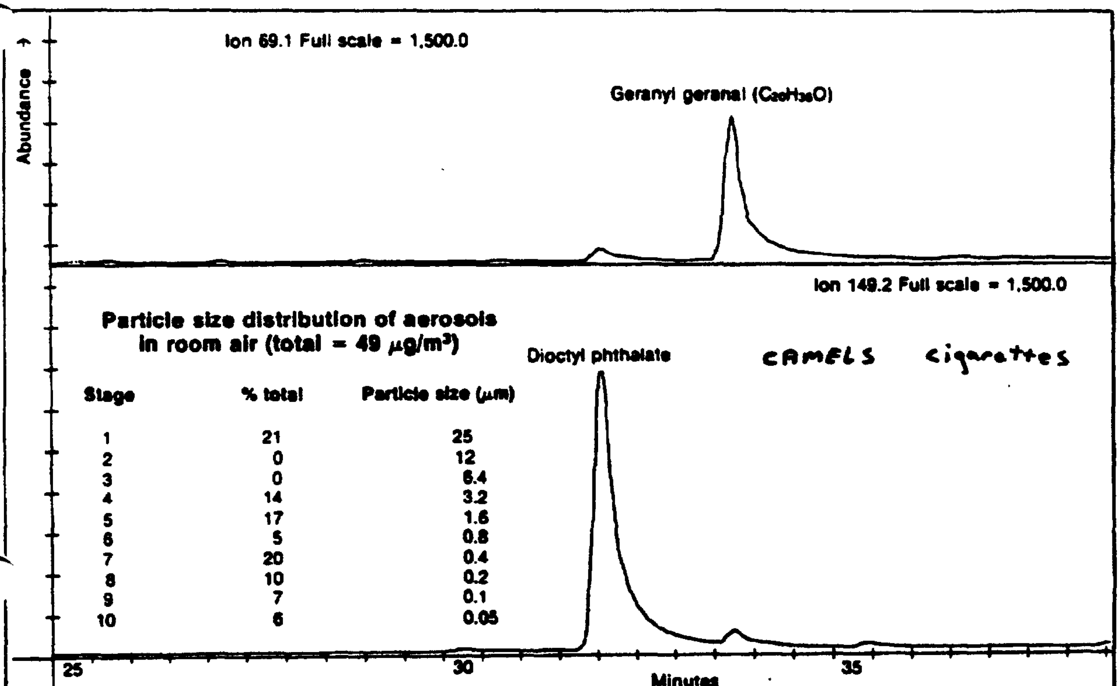
To evaluate the instrument, the author obtained several analyses of room air. With a 2 min. sample the total concentration measured was 49 $\mu g/m^3$ with the particle size distribution shown in the table. This compares to an average concentration for most indoor rooms of about 15 $\mu g/m^3$.

The next experiment undertaken was to

***SEM images** show particles collected on third stage during Feb. 28, 1978, sampling of Santiaguito Volcano eruption. Large particle has XRF pattern of rhyolite glass. Rings around particles are interpreted as residual acid coatings: small particles, acid droplets.*



***Effect of smog** in Los Angeles area on weather is shown by two 6-min. samples. Curve 1 is for sample obtained under warm, light wind conditions; concentration was 118 µg/m³ and mean particle diameter was 0.21 µm. Curve 2 was obtained for sample when wind was hot and brisk and smog was present. Concentration rose to 150 µg/m³, mean particle diameter to 0.25 µm.*



Particle size distribution of aerosols in room air (total = 49 µg/m³)

Stage	% total	Particle size (µm)
1	21	25
2	0	12
3	0	6.4
4	14	3.2
5	17	1.6
6	5	0.8
7	20	0.4
8	10	0.2
9	7	0.1
10	6	0.05

***Selected Ion Mass Spectral** (SIMS) run of 0.2 µm aerosol fraction from cigarette smoke using base ions shows relative amounts of two components. Crystal collector used was uncoated.*

observe the effect of cigarette smoke in the room. Drawing the smoke of the cigarette directly into the instrument for 15 sec, a total concentration of 91,064 µg/m³ was observed. (When disbursed, room smoking generally will raise a 15 µg/m³ concentration up to 100 µg/m³.) The particle size distribution revealed 75% of the smoke aerosol was contained in the 0.1 to 0.4 µm range.

Since the total amount collected in these three stages calculates to about 5 µg, and previous experiments indicated these aerosols were primarily liquid droplets, the quantity appeared to be feasible for conducting a GC/MS analysis. Therefore, the deposit on stage eight, an uncoated crystal, (0.2 µm comprising 44% of the total) was washed into 2 ml of hexane, condensed to 20 µl, and analyzed by GC/MS techniques.

The two major components detected were dioctyl phthalate and another compound that was identified by computer search as a terpenoid, geranyl geranal. The quantity of the dioctyl phthalate detected was about 0.2 µg, indicating it comprised about 10% of

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the aerosol collected on the crystal. The balance of the deposited aerosol was probably heavier tars, which were not analyzed by gas chromatography.

Altho great care was exercised at each step of this trace analysis, it is well recognized that when handling such small quantities of materials it is difficult to avoid artifacts. Should further experimentation prove this technique to be feasible, it opens the possibility of making many significant studies that would not be possible by other methods.

The signal output of the instrument is a set of 10 frequencies, one from each stage of the analyzer. The present design requires the operator to record the frequencies before and after a sampling period and then compute concentration and size distribution. It is clear that this procedure and the possibility of reaching saturation of a given crystal for dense aerosol samples are the two most serious drawbacks to use of the instrument.

California Measurements is in the process of developing a microprocessor-based control unit to do all these calculations automatically. Data will be digitally displayed either on the front panel or on a cathode ray tube and also will be printed.

The microprocessor also will perform another very important function — control the sampling time interval of the sampling valve so as not to exceed the linearity and allow saturation of any one stage. A number of housekeeping and self-test functions can also be programed to make the instrument easier to operate and maintain in the laboratory or field. ■

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