Technical Papers

Paper Chromatography for Identifying Air Pollutants

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During the first months of 1953, six samples of particulate material in outdoor air were obtained by filtration to determine the efficacy of paper chromatography for detecting pollution components. This preliminary report indicates a possible use of a relatively simple microanalytic tool for that purpose. Of greater interest is the accrued evidence that a derivative of acetic or formic acid in particulate form is characteristic not only of the San Francisco Bay Area air pollution but also of the effluent gases of several types of combustion.

The air-sampling station was on the roof of a three-story campus building. Samples of particulate material were obtained by drawing a large volume of air on each of 6 days through 15-cm circles of Whatman No. 40 filter paper. Figure 1 shows sample volumes and the resulting paper darkening caused by air contaminants. Since a preliminary interest concerned the possible presence in the contamination of lower fatty acids, a chromatographic method of Kennedy and Barker (*1*) was adopted.

In preparation for chromatography, the filters were extracted with dry ether, in some cases in a soxhlett apparatus, in others by overnight steeping at room temperature. The ether extracts were evaporated at room temperature to 15 ml, and then made to 25 ml with ammonia-saturated ether. This solution was evaporated to a small volume for application to the paper.

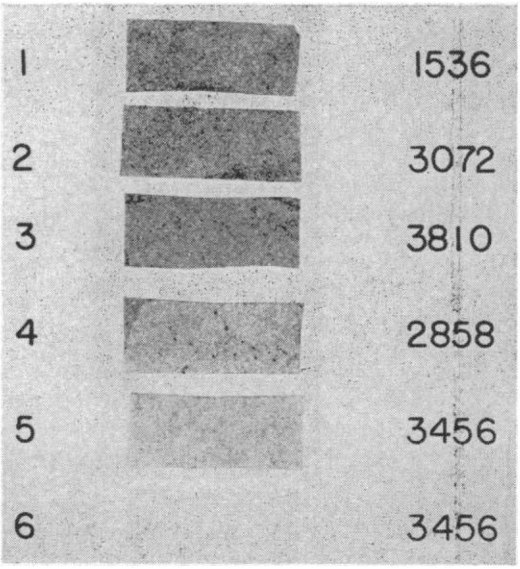

Fig. 1. Portions of Whatman No. 40 filter papers on which aerosol samples were obtained, each on a different day during daylight hours. The samples are numbered at the left; their volume (ft^3) is shown at the right. Samples 1 and 2 were taken in January, samples 3 and 4 in March, and samples 5 and 6 in May.

The developing liquid was 95 percent ethyl alcohol, containing 1 ml per 100 ml of aqueous ammonia. After developing the samples by the ascending technique on Whatman No. 1 paper, the paper was dried for about 1 hr in air and then sprayed with the bromphenol blue indicator described by Kennedy and Barker (*1*).

With each sample, a standard containing equal weights of formic, acetic, propionic, and normal butyric acids as the ammonium salts was developed. Using as little as 20 μg of the mixed standard, a separation of the several acids was obtained, except that formic- and acetic-acid spots nearly coincided at R_f 0.31 to 0.35. Figure 2 is a sketch of the separation achieved with samples 1 and 2.

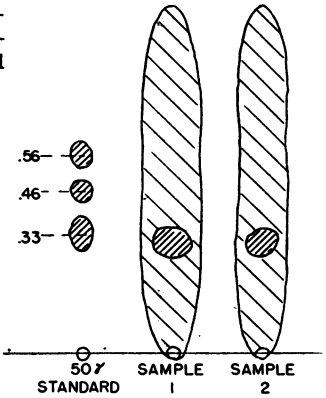

Fig. 2. Sketch of developed chromatogram. Elongated comets show spread of fluorescence.

In samples 1 to 4, acetate or formate was present. From spot-size comparison, the air concentration of equivalent acetate was estimated as follows: sample 1, 1 $\mu g/m^3$ of air; sample 2, < 0.5 $\mu g/m^3$; sample 3, < 0.5 $\mu g/m^3$; and sample 4, < 0.5 $\mu g/m^3$.

In no sample was an acid radical higher than the acetate detected. Under ultraviolet light an unidentified fluorescing material, in addition to the acid, appeared in each sample. Distribution of this fluorescence, which persisted 1 yr later, is indicated in Fig. 2. No acid was found in samples 5 and 6, although some fluorescing material was noted. These two samples, and especially sample 6, were appreciably less dark than the others (*2*).

Thus, a lower fatty-acid radical, detectable by chromatography, was present in several characteristic air-pollution episodes (*3*). This suggests that a relatively simple method of determination may be used to define the presence or absence of "smog." Reduction of visibility is not necessarily a criterion, since such an effect may be simply the result of water condensed on normally present nuclei.

It did not seem likely that either acetate or formate was present as the relatively volatile acid. Several laboratory experiments were run, filtering concentrations of acetic-acid or formic-acid vapor, readily detectable by odor, through Whatman No. 40 filter paper. In no case was acid recovered from the filter paper treated in the same manner as described previously. This was true even when carbonaceous smoke, made by incomplete combustion of benzene, was present in the mixture that was filtered.

It is possible that the acid radical found in the air samples was in the form of fine particles of one or more salts. Several acetates, including those of lead, calcium, sodium, copper, and magnesium, were prepared individually in solutions such that 0.1 ml contained 50 μg of acetate. Each of these preparations was evaporated to dryness and then taken up in ether saturated with ammonia, the latter solution being treated by the same chromatographic technique. In each case, nearly quantitative separation of acetate was achieved by spot-size comparison with a known standard solution. This indicates that any one of several acetate salts could have been present in the air samples and identified by the analytical procedure employed.

Since combustion seemed a possible source of the acid component detected in polluted air, the cooled gases from a number of combustion processes were sampled by filtration, either with Whatman No. 40 filter paper or with double-thickness extraction thimbles. The filters were dried at temperatures up to 100°C before analysis.

The gases thus sampled included engine exhaust of a relatively new automobile operating at idling speed (61 ft^3, showing only a trace of carbon); stack gas from an incinerator burning sawdust and a small amount of biological residues at a high temperature (10 ft^3, showing negligible free carbon and some finely divided fly ash); flue gas from a 75,000 Btu/hr natural-gas furnace (20 ft^3, showing no trace of carbon); and stack gas from a wood-burning fireplace (20 ft^3, showing appreciable carbon). From each of these combustion sources particulate acetates or formates were chromatographically separated in the following relative amounts: automotive exhaust, < 300 μg/m^3; incinerator, < 300 μg/m^3; gas fire, < 3000 μg/m^3; wood fire, > 3000 μg/m^3. There was no acid higher than acetic in any of the samples. Additionally, 18 ft^3 of natural gas contained no filterable acetate or formate. From each of these sources, except raw natural gas, a fluorescent, oily material was also extracted.

Because of the close approximation of the developed spots for formic and acetic acids, it cannot be said absolutely that all of the acidic material was one or the other. The spots found were at R_f 0.31 to 0.35. The data of Kennedy and Barker (*1*) show only acetic and formic acids at these low R_f values. Some additional data for the same type of analysis by Nair (*4*) indicate that a number of alkoxy acids are also at higher R_f values than 0.35. Thus, the substances filtered out of polluted air and determined by the procedure described are particulate one- or two-carbon acid radicals. Similar components are present in the effluent gas from combustion of several solid, liquid, or gaseous fuels. Additionally, it is probable that combustion in some cases is accompanied by synthesis of a small amount of the nonvolatile oil aerosol that was noted as fluorescent material on the chromatograms.

References and Notes

1. E. P. Kennedy and H. A. Barker, *Anal. Chem.* **23**, 1033 (1951).
2. On all sampling days, chosen because of visible haziness, the absolute and relative humidity was low, and the temperature was higher than ordinary. Records from two nearby stations show that wind velocities averaged less than 5 mi/hr except during the day of sample 6 when it was about 10 to 12 mi/hr.
3. J. D. Torrey has recently observed both lower fatty acid and fluorescent oil in a sample of filtered air from Denver, Colo.
4. J. H. Nair, *Anal. Chem.* **25**, 1912 (1953).

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Homogenizer for Continuous Homogenization

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In connection with the preparation of alkaline phosphatase from the microsome fraction of intestinal mucosa (*1*), it was desired to prepare homogenates in larger quantity than could be conveniently obtained with the conventional Potter-Elvejhem homogenizer. Consequently, a modification was made to permit a continuous passage of the material through the homogenizer.

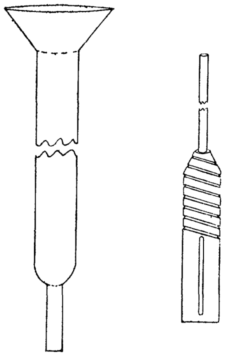

Fig. 1. Components of modified Potter-Elvejhem homogenizer.

The modified homogenizer is illustrated in Fig. 1. The barrel was constructed from a 25-mm Pyrex ignition tube, with a 10-cm length of 10-mm tubing sealed on one end to provide the outflow tube. The neck of a 250-ml Erlenmeyer flask was sealed to the other end of the ignition tube, and the bottom of the flask was removed to provide a reservoir for the material to be homogenized. The inside of the barrel was ground with a metal lapping tool and Alundum powder until the