region immediately above the layer results from an accumulation of fixing material. The dense surface layer has a thickness of about 0.25 μ when the total membrane thickness is 100 μ. The remainder of the film appears to be a spongy mass having a pore size on the order of 0.1 μ. The pore structure of the surface cast on the glass is like that of the interior.

For reference, a film cast from a solution of cellulose acetate and acetone and subsequently allowed to dry completely in air is shown in Fig. 2. This film is completely structureless at × 8000 (× 2100; 3.8 enlargement), and it is believed that the thin layer on the surface of the modified film (Fig. 1) is of the same physical constitution as the dense, air-dried film of Fig. 2.

During the several steps in the preparatory procedure it is impossible to remember the identity of each portion of the air-dried surface of the modified film. To effect this identification, a film was pressurized in the reverse osmosis apparatus at 1500 lb/in.^{2} During this step the surface cast toward the glass plate was embossed with the structure of the porous stainless steel backing plate used in the apparatus. This film was subsequently examined in the electron microscope. The dense surface layer was unchanged, while the opposite side contained the embossing, as shown in the lower half of Fig. 1. This montage was prepared from pictures of two nominally identical films and represents the observed structure; it is clear that the dense surface layer is the air-dried surface.

The gross improvement in the rate of water transmission of films prepared as suggested by Loeb and Sourirajan (*2*) is apparently due to the extreme thinness of the dense layer on the air-dried surface. Subsequent studies of the transmission rates of completely dense films 100 μ thick and the modified films show that the rates differ approximately by the inverse ratio of the thickness of this dense layer (that is, 100/0.25), supporting the concept that the permeation is a simple diffusion process and that the variation in permeation rate is a direct result of the effective membrane thickness.

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Sulfate Particulates: Size Distribution in Pittsburgh Air

Abstract. *Sulfate particles with diameters of less than 1.7 microns contribute approximately 40 percent by weight to total sulfate particulate in Pittsburgh air. The irritant nature of these particles and their small size and associated long atmospheric residence time, as well as the short half-life of sulfur dioxide in the atmosphere, suggest that particulate sulfate may be a better indicator of atmospheric pollution than sulfur dioxide.*

In 1955 Hemeon (*1*) suggested that zinc ammonium sulfate was in part responsible for the irritant properties of the fog which occurred during the acute air pollution episode at Donora, Pennsylvania, in 1948. Amdur and Corn (*2*) recently showed that aerosols of zinc ammonium sulfate, zinc sulfate, and ammonium sulfate produce a significant increase in pulmonary flow resistance in guinea pigs exposed to these aerosols for 1 hour. The double salt, which was the most irritant, was studied by generating four aerosol clouds and by characterizing them on a weight basis by their arithmetic-mean particle diameters of 0.29, 0.51, 0.74, and 1.4 μ. We found that the smaller the particles, the greater the irritant action, when the weight of test aerosol per unit volume of inhaled air remained constant. On the basis of the relevance of these findings to the potential effects of urban air pollution on human health, suspended particulate matter in Pittsburgh air was examined for its sulfate content as a function of particle size.

Air samples were collected on the roof of the Graduate School of Public Health during periods of low relative humidity in October and November 1963. A five-stage cascade impactor (*3*) was operated for 1 hour at a flow rate of 18 liters per minute. The collecting slides were coated with a thin film of Fisher Cello-seal; an HA Millipore filter was used for the final collection stage. The washings from slides at each collection stage were analyzed in a spectrophotometer by the quantitative turbidimetric reaction of $BaCl_2$ with sulfate at 420 mμ (*4*); $MgSO_4$ was used for calibration. The analytical procedure was sensitive to 0.5 μg of SO_4^{--} per milliliter in a cell whose pathlength was 40 mm. With the cascade impactor particles were fractionated according to their inertial properties and a range of sizes was collected on each impaction stage. For a given stage, half of the weight collected was associated with particles having diameters less than the mass median diameter. Table 1 shows the weight of sulfate collected and stage mass median diameters calculated for a particulate density of 2.0 g/cm^3 and an assumed reliability of the cascade impactor calibration (*3*). Approximately 35 percent of the sulfate weight is estimated to be associated with particles in the size range found by Amdur and Corn (*2*) to be irritant to guinea pigs—that is, less than 1.4 μ mass median diameter. Atmospheric sulfate concentrations, in the size range of irritant particles, were 0.7 to 7.1 μg/m^3, while concentrations, in the same size range, to which laboratory animals were exposed were 0.25 to 3.6 mg/m^3. However, the arithmetic mean of total suspended particulate concentrations in Pittsburgh from 1957 to 1961 was 0.19 mg/m^3, and a maximum concentration of 0.98 mg/m^3 occurred (*5*). It is not yet known whether these concentrations of mixed particulates, containing less than 5 μg of sulfate per cubic meter, are irritant to guinea pigs or man.

Table 1. Distribution of sulfate in 12 samples collected during October and November 1963. Total sulfate concentrations were 1.9 to 20.4 μg/m^3; relative humidity was 17 to 59 percent.

Cascade impactor stage	Stage mass median diameter (μ)	Total sulfate collected* (%)	Cumulative percentage (wt.) less than stage mass median diameter*
Filter		30.2 ± 8.9	
4th	1.7	24.8 ± 6.4	42.6 ± 9.7
3rd	3.2	18.6 ± 7.9	64.2 ± 10.2
2nd	6.0	14.8 ± 5.9	81.0 ± 7.9
1st		11.6 ± 5.3	94.2 ± 2.7

* Mean ± S.D.

The distribution of particle size associated with sulfate weight was mathematically transformed to a count distribution (*6*). A count distribution could also be obtained by observing particles in the optical microscope and equating their areas to those of calibrated circles in an eyepiece graticule. Approximately 90 percent of the sulfate particles are less than 1 μ in equivalent area diameter. Jacobs *et al.* (*7*) found that 84 percent of the suspended dust particles in outdoor air are 1 μ or less in equivalent area diameter. On the basis of Jacobs' work and the low terminal settling velocity of a 1-μ sphere of density 2.0 g/cm^3 in still air (7.0×10^{-3} cm/sec at 20°C and 760 mm-Hg pressure), it is reasonable to assume that sulfate particles in Pittsburgh air remain suspended for long periods of time. Sulfate particles are also hygroscopic and presumably enlarge as the relative humidity of the air increases and become desiccated as the relative humidity decreases.

Sulfate particles can be formed by the photochemical oxidation of sulfur dioxide in the atmosphere (*8*). In natural sunlight in a concentration range of 5 to 30 parts per million, the photochemical oxidation of sulfur dioxide proceeds at 0.1 to 0.2 percent per hour (*9*). In the presence of fog droplets and a manganese catalyst, the oxidation rate can be as high as 1 to 2 percent per minute (*10*). The rate of formation of ammonium sulfate from sulfur dioxide and ammonia gases is proportional to the surface area of the fog droplets down to a diameter of 0.1 mm (*10*). Finally, the average life of a molecule of sulfur dioxide in fog or mist is estimated to be 3 to 4 hours (*11*).

Because of the short life of sulfur dioxide in the atmosphere and the size and associated irritant nature of particulate sulfate formed by its oxidation, suspended particulate sulfate may be a better indication of urban air pollution than sulfur dioxide.

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Tritium-Hydrologic Research: Some Results of the U.S. Geological Survey Research Program

Abstract. *In general tritium is of limited usefulness as a tool in hydrologic studies because the tritium content of ground water, as a result of radioactive decay, becomes too low to be detectable after about 50 years. Nevertheless, a unique study was made of the hydrologic cycle of small stream basins in Wisconsin and New Jersey on the basis of measurements relative to the peak of tritium fallout in the spring of 1958. The continental and the coastal basins received approximately the same tritium fallout. Approximately 30 percent went into ground-water storage, the remainder being exported as runoff and evapotranspiration. The mean residence time for ground-water recharge for the two basins was 45 and 30 days, respectively.*

From January 1958 to July 1962 I was in charge of the U.S. Geological Survey research program established to explore the value of the radioisotope tritium as a hydrologic tool in ground-water studies. Its 12.26-year half-life suggested that it might be of value as a means of dating ground water. Tritium is produced in huge quantities in hydrogen bomb tests, and the many such bomb tests since 1954 have greatly increased the levels of tritium in precipitation throughout the United States. As a water molecule (HTO), tritium is apparently not subject to selective adsorption by soil or clay particles or to exchange with other elements; therefore, it should represent an ideal water tracer. One publication on the results of the first project to be completed is now in print (*1*). The full results of the research program will be published later; however, certain highlights of the results of the research, involving interpretations for which I am responsible, are believed to be sufficiently timely and of broad enough interest to be presented to the general scientific community at this time. This report should be of further interest in its description of the role of W. F. Libby in the planning of a scientifically fruitful and unique peaceful use of atomic energy in the field of hydrology.

Thatcher (*2*) has concluded that the pre-hydrogen-bomb, or pre-1954, levels of naturally produced tritium in precipitation ranged from 8–10 tritium units (1 tritium unit, or T.U., is one tritium atom per 10^{18} hydrogen atoms) in the continental interior of the United States to 3–5 tritium units along the Atlantic and Pacific coastal margins and to 2 tritium units in southern Florida.

The relatively short half-life of tritium (12.26 years) places a serious limitation on its usefulness for dating ground water. In ground water older than 50 years in the continental interior and 25 to 35 years old in the seaboard regions, so much of the original tritium has been lost through radioactive decay that none is detectable by tritium analysis. About 90 to 95 percent of the available ground-water reserves in the United States are probably older than 50 years; therefore, absence of detectable tritium in ground water has little or no bearing on the general problem of ground-water availability. Only ground water in recently recharged areas can be expected to contain measurable amounts of tritium. When such water is pumped from a well, particularly one without casing, the ground water drawn into the well from the upper part of the aquifer may contain over 100 tritium units, whereas that drawn into the well from the lower parts of the aquifer may contain none. The pumped water is thus a mixture of water of different ages and tritium contents, and to assign a definite age to a mixture of such water is meaningless.

In early 1958, at the beginning of the tritium research program, W. F. Libby, at that time a member of the