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Publication Date

1973-09-01

Presented at
Summer Institute on Energy:
Resources, Utilization, and Environmental
Impact, Berkeley, California,
June 25-August 3, 1973

LBL-2162

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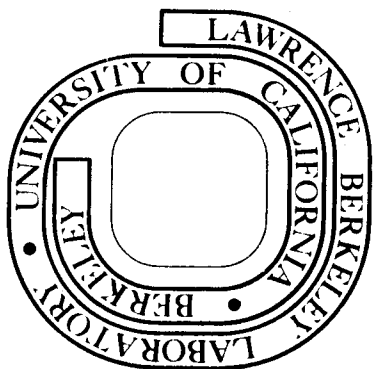
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September 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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LBL-2162

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MEASUREMENT OF ATMOSPHERIC SULFATE*

by

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The attribution of serious health consequences to atmospheric sulfate has stimulated interest in the analysis of particulate sulfate in ambient air.¹ Sulfate particulate has also been implicated in problems involving visibility.^{2,3,4} Most urban atmospheric sulfur originates with sulfur dioxide (and much smaller quantities of sulfur trioxide) formed during the combustion of fossil fuels. The gaseous oxides of sulfur are converted in a relatively brief period of time (days) to particulate sulfate. Average sulfate concentrations in urban air are on the order of approximately $2 \times 10 \mu\text{g}/\text{m}^3$. The high toxicity of sulfate may be due to the ability of the particulate to penetrate deeply into the lungs whereas the effects of gaseous sulfur dioxide are largely limited to the upper respiratory tract and eyes.

Sulfate particulate, as other particulate pollutants, is usually collected from ambient air with high volume (1 to 21 m³/min) samplers⁵ or impactors.⁶ The collected particulate is then analyzed by various means

*Information for this report was prepared for the survey, "Instrumentation for Environmental Monitoring AIR," LBL-1, Vol. 1. This work was supported by the National Science Foundation and performed in facilities provided by the U.S. Atomic Energy Commission.

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including ESCA, optical methods based on methylthymol blue, turbidimetry, or nephelometry. All procedures other than ESCA require that the sulfate be dissolved prior to analysis, therefore only soluble sulfate is measured.

Electron spectroscopy for chemical analysis (ESCA)^{7,8} is the most sensitive analytical technique at the present time. After collection of as little as a monomolecular layer of particulate on a flat surface, ESCA can detect 10^{13} sulfate sulfur atoms per square centimeter.⁹ This procedure permits the analysis of samples collected from air during relatively brief periods of time, does not rely on chemical reactions which may be subject to complication, does not require that the particulate sulfate be soluble, and is non-destructive. A limitation is that sulfate sulfur must account for a minimum of 1% of the mass of the monolayer.⁹ Although more sensitive than any other procedure, ESCA is new and unknown to many air pollution laboratories, the equipment is expensive, and the technique is still something of an art practiced in very few laboratories. These limitations should not, however, prevent the application of ESCA for sulfate analysis. A feasible approach would be to submit samples collected for analysis to those few laboratories which do have the requisite equipment and expertise.

Automated procedures¹⁰ employing instruments such as the Technicon AutoAnalyzer¹¹ provide a routine colorimetric procedure for sulfate determination.

"The reagent containing equivalent amounts of barium chloride and methylthymol blue is reacted with the sulfate ion. A barium dye chelate is prevented by maintaining a pH of 2.8. After the reaction between the sulfate ion and the barium ion, an excess of

methylthymol blue exists, equivalent to the amount of sulfate present. After the pH is increased to 12.4, the unreacted barium forms a chelate with the dye and the excess dye, which is equivalent to the sulfate, becomes yellow and can be determined colorimetrically."¹¹

The AutoAnalyzer is described more fully in Reference 11. The range of this analysis is approximately 0.3 to 45 $\mu\text{g SO}_4^-/\text{m}^3$ air; sensitivity is about $\pm 0.3 \mu\text{g SO}_4^-/\text{m}^3$ air.¹²

Turbidimetry¹³ is one of the standard methods¹⁴ of sulfate analysis for which a modification,¹⁵ the parallel photometric analysis technique (GeMSAEC), has recently been suggested. Barium chloride or 4-amino-4'-chlorodiphenyl hydrochloride (CAD) is employed to precipitate the sulfate. The procedure involves a comparison of light transmitted by the resulting turbid mixture with light transmitted by turbid mixtures formed from standard sulfate solutions. Since turbidity is dependent not only upon the mass of solid in a given volume of fluid, but also upon the distribution of particle sizes, it is imperative that the distribution of the particle sizes in the standard and test runs be identical. Herein lies one of the major problems of turbidimetric analysis, a problem addressed by the parallel photometric analysis technique. Coleman¹⁵ claims precision and accuracy of $\pm 1\%$ at 4 $\mu\text{g SO}_4^-/\text{ml}$ test solution; using the collection and solution procedures described in Reference 11, this would correspond to about 1 $\mu\text{g SO}_4^-/\text{m}^3$ air.

Nephelometric techniques are also used to determine sulfate in ambient air.^{16,17} Although nephelometry can be more sensitive than turbidimetry, nephelometry suffers from the same main disadvantage, that is, the difficulty of reproducing a distribution of particle sizes. Modifications similar to those of Coleman¹⁵ may be appropriate here also.

Procedures which have recently been proposed for analysis of sulfuric acid in ambient air may be subject to modification for analysis of total particulate sulfate. Among these are the barium chloranilate method¹⁸ and flame photometry.^{19,20}

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