L-21170, 1974.3 is NGS line L-23315, and 1976.5 is Riverside County line No. 603; (iii) Mecca to Frink Quarry: 1976.4 is NGS line L-24071, and 1977.3 is USGS Summary Book PV 995U; (iv) Frink Quarry to El Centro: 1972.1 is NGS line 22606, 1974.1 is NGS line L-23243, and 1977.0 is NGS line L-24130.

13. We thank R. O. Castle for encouraging us to study vertical tectonic deformation in southern California; T. C. Hanks and R. A. Page for suggesting that large tilts in the Salton depression, as interpreted from geodetic data, might be manifested in different ways; and B. E. Lofgren for informing us that water-level data were available. We thank R. Spencer and W. Norried of the Coachella Valley Water District and D. A. Twogood of the Imperial Irrigation District who provided water-level data, S. M. Reese (National Geodetic Survey) who provided recent releveling data, M. R. Elliott who guided us in utilizing the leveling data, and M. J. S. Johnston and J. Ohl who gave helpful suggestions on the data and the manuscript. Publication approved by the Director of the U.S. Geological Survey, 2 January 1979.

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Dimethyl and Monomethyl Sulfate: Presence in Coal Fly Ash and Airborne Particulate Matter

Abstract. *Dimethyl sulfate and its hydrolysis product monomethyl sulfate have been found at concentrations as high as 830 parts per million in fly ash and in airborne particulate matter from coal combustion processes. This discovery poses a new environmental problem because of the mutagenic and carcinogenic properties of these compounds.*

Much effort and money have been and are being expended to reduce the amount of airborne particulate sulfate generated by fossil-fuel combustion. Most of this activity has occurred because epidemiological studies suggest that long-term, low-level exposure of human populations to the sulfur compounds in airborne particulate matter is detrimental to health. However, the results of these epidemiological studies are still in question, and there has been no demonstration of any long-term toxic effects of any of the sulfur compounds known to be present in airborne particulate matter (*1*).

We have reported the presence of organic derivatives or adducts of sulfur oxides in airborne particulate matter collected in urban environments or from coal-burning facilities (*2*). These unidentified organic derivatives and compounds of sulfur in an oxidation state less than +6 usually account for 5 to 15 percent of the total sulfur present in such samples. The balance of the sulfur is present as salts of SO_4^{2-}, salts of HSO_4^-, or H_2SO_4. In the process of isolating and identifying the organic derivatives of sulfur oxides, we have found dimethyl sulfate [$(H_3CO)_2SO_2$] and its hydrolysis product monomethyl sulfate ($H_3COSO_3^-$) to be present in fly ash and in airborne particulate matter originating from coal combustion. To our knowledge, this is the first report of the presence of short-chain alkyl sulfates in the environment except in the vicinity of industrial plants where these compounds are manufactured or used (*3*). Although these two compounds constitute only about 0.5 percent of the total sulfur present in the samples, we believe this discovery is important because of the proved mutagenic and carcinogenic properties of dimethyl sulfate (*4*).

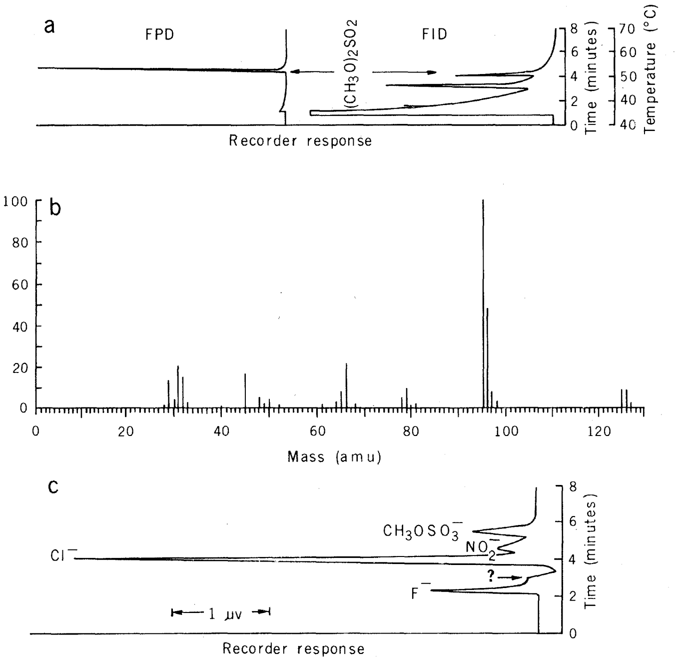

Fig. 1. Data from the methanol extract of fly ash: (a) The FID-FPD gas chromatogram (*6*). (b) Electron-impact mass spectrum of the peak labeled $(CH_3O)_2SO_2$ in (a) (*6*). (c) Ion chromatogram after the evaporation of methanol followed by dissolution in water (*10*).

Samples of fly ash were collected directly from the flue line (gas temperature ~110°C) of a modern chain-grate, stoker type, coal-fired heating plant which burns about 20,000 tons of coal per year. The coal was low-sulfur (0.5 percent), high-ash (14 percent) coal from southern Utah. No size fractionation was attempted on these samples. The plant meets the emissions requirements of the Environmental Protection Agency but has no emission controls except an extended flue line to trap the fly ash and a stack 50 m tall.

We collected the total suspended airborne particulate matter on acid-washed, quartz-fiber filters by using a high-volume sampler with a constant flow controller located on the roof of a building 125 m from the stack and 30 m below the top of the stack. The sampler was operated for from 2 to 5 days to collect each sample during inversion conditions when there was little or no wind. The particulate matter collected was assumed to be emissions from the stack of the heating plant as there were no other major emission sources within 15 km of the plant.

The air particulate and fly ash samples were first extracted in a Soxhlet apparatus with methylene chloride to remove organic materials which interfered with the dimethyl sulfate determination. The fly ash from the flue line was found to contain very low concentrations of organic compounds soluble in methylene chloride and therefore the methylene chloride extraction was omitted. No dimethyl sulfate was extracted from any of the samples with methylene chloride. The samples were then extracted with methanol, some portions by Soxhlet extraction and some in an ultrasonic bath at room temperature (*5*).

The methanol extracts were analyzed by gas chromatography with a glass capillary column and both a flame ionization detector (FID) and a sulfur-specific flame photometric detector (FPD) (Fig. 1a). Dimethyl sulfate was identified by comparison of the retention time with that of pure dimethyl sulfate standard (Eastman, reagent grade) and by gas chromatography-mass spectrometry (*6*)

(Fig. 1b). Dimethyl sulfate was also identified in the fly ash samples by gas chromatographic-mass spectral analysis of nitromethane and acetonitrile extracts of the sample, which demonstrated that dimethyl sulfate was not formed as an artifact during methanol extraction.

The concentration of dimethyl sulfate in methanol slowly decreased with time, probably because of reaction with the solvent (reaction 1) or hydrolysis with residual amounts of water present in the solvent (reaction 2) (*7*):

$$(CH_3O)_2SO_2 + CH_3OH \rightarrow (CH_3)_2O + CH_3OSO_3H \qquad (1)$$

$$(CH_3O)_2SO_2 + H_2O \rightarrow CH_3OH + CH_3OSO_3H \qquad (2)$$

Reaction 2 would be expected to occur in the environment, and the possible presence of monomethyl sulfate in the samples was also investigated. In the hydrolysis of dimethyl sulfate by water, the first methyl group is removed much more rapidly than the second. We found that dimethyl sulfate in water, dilute acid, or dilute base was completely hydrolyzed to monomethyl sulfate in a 24-hour period, but the monomethyl species was stable over a period of several weeks. These results are consistent with the results of earlier studies (*8*).

We analyzed aqueous solutions for monomethyl sulfate by ion chromatography (IC) (*9, 10*) (Fig. 1c). We quantified the yield by constructing a calibration curve from the chromatographic peak heights, using potassium monomethyl sulfate (Eastman, reagent grade). Although aqueous solutions of monomethyl sulfate were stable for long periods of time, in the presence of fly ash low concentrations were over 90 percent hydrolyzed to sulfate overnight. Furthermore, direct extraction of the fly ash samples with water gave lower values for monomethyl sulfate than extraction with methanol followed by IC analysis for monomethyl sulfate. Therefore, samples were first extracted with methanol and evaporated to dryness, and the residue was dissolved in water and immediately analyzed by IC. The absence of monomethyl sulfate in methanol solutions made by reextracting fly ash with methanol and also the presence of monomethyl sulfate in a water or acetonitrile extract provide strong evidence that the monomethyl sulfate is not an artifact of the extraction procedure.

The quantitative results of our measurements are given in Table 1. The concentrations of the methyl sulfate species measured are undoubtedly lower limits of the actual amounts present, since an appreciable amount may be hydrolyzed to SO_4^{2-} during the extraction procedure. Higher values were generally obtained with shorter extraction times (20 minutes) and immediate (within 1 hour) chromatographic analysis.

Table 1. Concentrations (micromoles per gram) of dimethyl sulfate and monomethyl sulfate found in non-size-fractionated fly ash and airborne particulate matter from a coal-fired heating plant.

Sample*	Dimethyl sulfate	Monomethyl sulfate
Fly ash 1	0.74	0.44
Fly ash 2	0.84	1.9
Ambient 1	0.07	0.22
Ambient 2	0.34	0.88

*Samples fly ash 1 and fly ash 2 are two separate samples (not size-fractionated) collected directly from the fallout in the flue line just ahead of the stack. Samples ambient 1 and ambient 2 are total suspended particulate samples collected over 2 and 5 days, respectively, in the near vicinity of the heating plant as outlined in the text.

To investigate the extent of conversion of methylated sulfate compounds to sulfate and methanol during the extraction procedure, a sample of fly ash 2 was extracted in water and analyzed for methanol by gas chromatography (*11*). Immediately after extraction, the solution contained 0.17 μmole of methanol per gram of ash extracted. After storage at room temperature for 24 hours, the solution contained 3.4 μmole of methanol and 0.07 μmole of monomethyl sulfate per gram of ash extracted. The relatively small amount of methanol initially present in the extract and the agreement between the final concentrations of methanol expected (3.6 μmole/g, calculated from data in Table 1) and that found (3.4 μmole/g) confirm the accuracy of our analytical techniques.

In order to determine whether the production of methylated sulfates is unique to the heating plant described, we analyzed a size-fractionated fly ash (*12*) collected downstream from the electrostatic precipitator of a large western coal-fired power plant. Monomethyl sulfate was identified at concentrations of 0.2 to 7.4 μmole/g, with the highest concentration present in the particulate matter of smallest (< 2.2 μm) size. Because of the limited amount of material available, we did not analyze for dimethyl sulfate. We have also identified dimethyl and monomethyl sulfate at comparable concentrations in samples collected in an ongoing study in the plume of a different large, coal-burning power plant.

The results indicate that the concentration of methylated sulfates may be as high as 1000 parts per million in primary respirable particulate matter (< 1 μm) from coal-fired facilities. Furthermore, the results from airborne particulate matter samples indicate that these compounds can have a residence time of hours to days in the ambient atmosphere.

Because dimethyl sulfate is known to decompose at its boiling point of 188°C, it must be formed downstream of the combustion chamber (*13*). Thermodynamic data show that dimethyl sulfate could be formed exothermically from major components of the flue gas as shown in reaction 3 (*14*):

$$5CO(g) + SO_2(g) + 3H_2O(g) \rightarrow (CH_3O)_2SO_2(\ell) + 3CO_2(g) \qquad \Delta H_{25^\circ C} = -77.7 \text{ kcal/mole} \qquad (3)$$

where ΔH is the heat of the reaction. If this is the mechanism for formation of the methylated sulfate compounds, then one would also expect to find these species produced as a result of the combustion of other sulfur-bearing fuels.

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5. The Soxhlet extractions were done with 300 ml of solvent for a period of 24 hours. Extraction in the ultrasonic bath was done with 125 ml of solvent for 30 minutes.
6. We used a gas chromatograph (Perkin-Elmer Sigma 2) equipped with both FID and FPD. The column was a glass capillary (28 m long by 0.29 mm in inside diameter) coated with SE-52 (0.35-mm film thickness). The oven was programmed from 50° to 125°C at 5°C per minute (2-minute initial time after injection). We used a gas chromatograph-mass spectrometer (Hewlett-Packard 5982A) with a data system (Hewlett-Packard 5934A). Chromatographic conditions were the same as those described above. The mass spectrometer was operated at an ionizing energy of 70 eV and was continuously scanned from 15 to 350 atomic mass units (amu) at the rate of 3 amu/sec.
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10. We used an ion chromatograph (Dionex model 10) with a 500-mm anion separator column with 1.2 m*M* Na_2CO_3–1.5 m*M* $NaHCO_3$ eluent at a 30 percent pump rate. Under these conditions, $CH_3OSO_3^-$ was well separated from NO_2^- (Fig. 1c); NO_2^- does not separate from monomethyl sulfate in this instrument with the usual anion eluent (*9*) which is twice as concentrated nor does it separate with Na_2CO_3-NaOH or borate eluents.
11. We used a gas chromatograph (Hewlett-Packard 5720A) equipped with an FID. The glass column (1.2 m long by 6.3 mm in inside diameter) was packed with 35/60 mesh Tenax. The carrier gas was helium, at a flow rate of 30 ml/min. The oven was run isothermally at 100°C.
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A Palladium–Palladium Oxide Miniature *p*H Electrode

Abstract. *A wire-form miniature palladium-palladium oxide electrode has been fabricated for* pH *measurement. The electrode exhibits a super-Nernstian behavior and gives a mean* pH *response of 71.4 millivolts per* [pH] *(standard deviation, 5.2 millivolts). Uncorrected zero current potential values can be used to determine the* pH *value of the medium to within 0.012* pH. *The electrode should find applications in biological, medical, and clinical studies.*

Miniature or microminiature sensors are needed for *p*H measurements of blood and extracellular fluids as well as for laboratory animal micropuncture studies. Very small glass electrodes have been fabricated for these applications (*1*); however, the fragile nature and thrombogenic characteristics of the glass membrane have limited in vivo applications of this sensor. Antimony-antimony oxide and quinhydrone electrodes have also been used, but their stability is relatively poor (*2*). Coon and his coworkers have reported that palladium oxide (PdO) can be used for *p*H sensing in a pCO_2 sensor (pCO_2 is the partial pressure of CO_2) (*3*), but PdO has not been directly used as a miniature *p*H sensor.

In biological and medical investigations, there is a need for a continuously operating, miniature *p*H electrode with reasonable reliability, stability, sensitivity, and durability. We have fabricated a Pd-PdO wire-form electrode which is *p*H-sensitive both in various buffers and in whole blood. The sensor's diameter is either 0.25 or 0.5 mm. The zero current potential measured between the sensor and an Ag-AgCl reference electrode in a test medium exhibits a linear relation between the potential and the *p*H value of the medium. Its *p*H response is reproducible to within 0.25 *p*H without calibration, and it should find use in a wide range of biological and medical applications.

Betteridge and Rhys (*4*) have demonstrated that a thin PdO surface film can be formed when Pd metal is heated to 973 K in air. This film is too thin to form a stable electrode. We have taken an alternate electrochemical approach in which pure Pd wire (0.25 or 0.5 mm in diameter and approximately 90 mm long) served as the anode and pure Pt wire (0.25 mm in diameter) was used as the cathode. A mixture of a 98 percent $NaNO_3$ (by weight) and 2 percent LiCl was used as a molten-salt electrolyte (melting point, 583 K). Empirically, we found the best performing Pd-PdO *p*H electrode was formed with an anodic potential of 5.9 to 6.2 V, a current density of 20 mA/mm^2, and an oxidation time of 90 seconds. A well-oxidized Pd wire had a velvety black appearance. When a thinner oxide layer was formed, the oxide film was light gray or brown. After oxidation, the electrode was stored in a phosphate buffer (*p*H 7) for a minimum of 24 hours. This preconditioning of the electrode enhanced its performance.

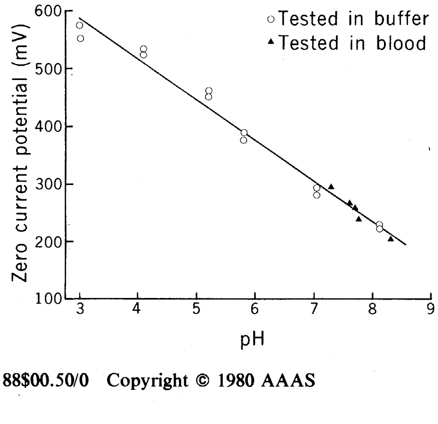

Fig. 1. Calibration curve of a Pd-PdO *p*H electrode in buffer solutions and whole blood at 310 K. The potential was measured versus an Ag-AgCl electrode.

The Pd-PdO electrode reacts with H^+ according to the reaction

$$PdO + 2H^+ + 2e^- \rightleftarrows Pd + H_2O \quad (1)$$

The activities of PdO and Pd for this electrode are unity; thus the *p*H response in the presence of a large quantity of water should be given by the Nernst equation

$$E = E^0 - \frac{RT}{F}\,[pH] \quad (2)$$

where E is the measured zero current potential, E^0 is the standard-state potential, R is the gas constant, T is the absolute temperature, and F is the Faraday constant.

Electrodes were calibrated in buffer solutions and in whole blood with a standard Ag-AgCl electrode as a reference. The electrical source impedances of the electrodes were nominally 600,000 ohm/mm^2; thus for our sensors which had an active length of 38 mm, the source impedance was approximately 10,000 ohm. This meant that the zero current potential between the Pd-PdO and the reference electrodes could be measured with an ordinary electronic voltmeter or high-input impedance chart recorder.

Figure 1 shows the response of a Pd-PdO electrode in buffer solutions and blood, the latter over the physiological *p*H range of 7 to 8.2. The absolute values of the zero current potentials are reported. The reproducibility of the *p*H response taken at different times indicates that this electrode does not have an asymmetric potential such as the glass electrode and thus frequent recalibration is not necessary. The super-Nernstian behavior may indicate the interaction between H^+ and the electrode surface.

Ten electrodes gave a mean *p*H response of 71.4 mV/[*p*H] (the standard deviation is 5.2, and the coefficient of variation is 7.3 percent). Linear regression analysis gave a mean correlation coefficient of .995. At *p*H = 6.98, the ten electrodes gave a mean absolute potential of 313.2 mV (standard deviation, 3.7). This corresponded to a difference of 0.012 *p*H.

The time response of the electrode, determined from step changes of *p*H in phosphate buffer solutions, was on the order of 0.5 second. No observable hysteresis effects were seen throughout the test. It is difficult to say whether this response time was limited by solution mixing or the electrode.

The theoretical temperature effect on

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