To be presented to the Division of Environmental Chemistry, American Chemical Society, Honolulu, Hawaii, April 1-6, 1979

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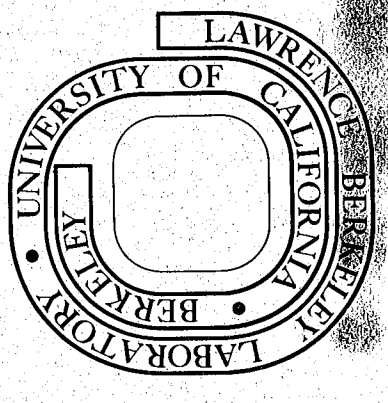
J. M. Jaklevic, R. S. Adachi, and F. S. Goulding

September 1978

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48



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AN AUTOMATIC PARTICULATE SULFUR MONITOR USING A DICHOTOMOUS SAMPLER AND X-RAY FLUORESCENCE ANALYSIS*

J. M. Jaklevic, R. S. Adachi, F. S. Goulding,
D. A. Landis, and B. W. Loo
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

A combined air particulate sampler and elemental sulfur analyzer has been developed for continuous monitoring of fine particulate sulfur. It consists of a dichotomous sampler, continuous tape membrane filter system, and single-channel wavelength dispersive x-ray fluorescence spectrometer. The unit operates automatically under microprocessor control and is designed to be transportable to remote sampling sites. Calibration data are retained within the microprocessor program and the concentrations are available shortly after the completion of the sampling period.

The dichotomous sampler is a single stage unit operated at a flow of 16.7 l/m and a 2.5 micron cutpoint. It is adapted from a recent design and is characterized by extremely low losses and sharp cutpoint behavior.[1] Since the sulfur analysis is performed only on the fine particle fraction, the coarse particles are collected on a large area cellulose filter which need be changed only occasionally during periodic service of the instrument. The fine-particle fractions are collected on 1.0 micron pore size Teflon membrane filters. These are mounted at 7.62 cm intervals on a 3.5 cm wide continuous strip. The active area of the filters is defined by 1.11 cm diameter holes; additional 0.5 mm holes are punched in the tape for the optical position sensor. A 17 cm diameter roll of the filter strip can accommodate approximately 1,000 samples.

The x-ray fluorescence spectrometer employs a low-power (30 watt), air-cooled Ag anode x-ray tube. The excitation radiation is incident on the underside of the Teflon membranes on the opposite side from the deposit. This allows the Be entry window to the x-ray spectrometer to be placed in close proximity to the particulate deposit thus minimizing x-ray absorption due to the short air path. The spectrometer employs Söller slits, Ge $\langle 111 \rangle$ crystal, and a gas-filled proportional counter. The slits are adjusted to view a sample area 1 cm x 1 cm. The entire assembly is operated in a hermetically sealed chamber with a He atmosphere to reduce attenuation. The energy resolution is 13 eV for the 2.31 keV sulfur K_α x-ray. This represents a compromise between maximum efficiency and the necessity of resolving the sulfur K_α line from the lead M_α peak which is 35 eV higher in energy.

The use of thin Teflon filters (approximately 1 mg/cm^2) provides several advantages for x-ray fluorescence analysis. The fluorescence excitation, which consists mainly of silver L x-rays at 3 keV, are transmitted through the filter with 92% efficiency. Similarly, the maximum possible correction for x-ray absorption effects due to penetration into the filter is 4%. Since the dichotomous sampler ensures that the particle size will be less than 2.5 microns, the errors due to absorption effects will be minimal.

*Footnotes

Normal operating procedures involve the acquisition of samples for time intervals ranging from 1 to 24 hours. At the end of this interval, the unit is cycled; the exposed filter advances to the analysis location and a clean filter is located for the next sampling interval. The analysis period is normally set much shorter than the sampling period. The sampler is equipped with a flow-controller and filter overload sensor which causes the sampler to cycle to the next filter if an episode of high particulate concentrations occurs. The control program keeps track of the shortened sample interval and includes this correction when converting the sulfur concentration to ngm/m^3.

Measurements of background and sensitivity for the spectrometer indicate a minimum detectable limit (3 σ) of 130 ngm/m^3 for a 1 hour sample period followed by a 30 minute analysis. Longer sampling intervals result in correspondingly lower detection limits; for example, a 24-hour sample would give a detection limit of 5 ngm/m^3. The accuracy of the results is determined mainly by the calibration standards and the magnitude of possible absorption effects. We estimate an accuracy of 5% or less. Improved sensitivity for the instrument could be achieved most easily by increasing the efficiency of the x-ray fluorescence spectrometer which is presently limited by the angular divergence necessary for 13 eV resolution. The use of curved crystal x-ray optics to replace the existing system could result in an efficiency increase of 5 to 10 times. The present x-ray tube design does not permit the minimum possible spacing between anode and sample. A factor of four increase in excitation efficiency could easily be achieved with slight modifications. The resulting sensitivity would reduce the minimum detectable limit by a factor of five or better. This would permit the analysis of very short-term samples with adequate sensitivity. For example, the detectable limit for a 5 minute sample would be approximately 300 ngm/m^3.

The use of the continuous tape sampler together with an automatic controller allows the possibility of performing additional measurements on the collected particulate samples. The Pb concentration can be measured with a slight adjustment in the wavelength spectrometer. Optical attentuation and total mass determinations with a beta-gauge could both be incorporated into a similar instrument.

References

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*Footnotes

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720