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DUAL ATMOSPHERIC TRACER TECHNIQUES FOR DIFFUSION STUDIES USING PHOSPHORESCENCE-FLUORESCENCE ANALYSIS

By

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DUAL ATMOSPHERIC TRACER TECHNIQUES FOR DIFFUSION STUDIES USING PHOSPHORESCENCE-FLUORESCENCE ANALYSIS

INTRODUCTION

Recently a method utilizing electronic counting of phosphorescence was reported by the author[1] for the quantitative detection of zinc sulfide pigment which is used as an atmospheric tracer at Hanford in the study of atmospheric diffusion under various meteorological conditions. Such information is not only required in appraisal of air pollution problems, but also provides basic information required to understand the turbulent diffusion processes in the atmosphere. The effect of height of release on downwind dosage patterns can best be studied through simultaneous release of two different tracer materials at two heights thus providing a direct comparison during the same atmospheric conditions. Experiments utilizing a single tracer rely on gross meteorological measurements to compare between experiments. The dual tracer technique should reduce the number of experiments required to produce definitive results.

The requirement is, then, that simultaneous release of two tracers take place at two locations. A further criterion restricts the tracers to materials which behave identically, or as nearly so as possible, in the atmosphere. Considerable work has been done in an attempt to utilize two types of zinc sulfide pigments whose phosphorescence decay or spectral emission is significantly different. However, only partial success has been obtained because of limitations on particle size, aqueous and light stability, broad phosphorescent spectral distributions, and rather small differences in decay characteristics. In all cases measured, the significant cross interference would limit the sensitivity and restrict the usefulness of the technique. Work is continuing along this line in an effort

to improve the method; however, recent work by Robinson, et al.,[2] has indicated the value of fluorescein (sodium salt) as a tracer for atmospheric dispersion studies and, because of the more common use of zinc sulfide pigment as a tracer, has demonstrated that the fluorescein generation can be controlled so that its air transport is very similar to that of zinc sulfide.

The present work describes the feasibility of using fluorescein simultaneously with zinc sulfide as tracers in atmospheric dispersion and transport studies. Currently, zinc sulfide detection requires collection of the dispersed particles on molecular filters* and quantitative measurement by counting phosphorescence emission. As little as 5×10^{-9} grams of zinc sulfide may be reliably detected on either clean or dirty filters. Addition of as much as 10^4 times as much fluorescein will not have a significant effect on the zinc sulfide sensitivity. The fluorescein fluorescence may then be detected photometrically with a sensitivity of 1×10^{-9} grams in the presence of normal zinc sulfide concentrations encountered and under almost all dirt contamination conditions found experimentally.

SUMMARY AND CONCLUSIONS

An analytical technique was developed for wind studies to determine the effect of height of release on ground level dosage patterns.

Two atmospheric tracers, zinc sulfide and fluorescein, may be simultaneously dispersed at varying altitudes and collected downwind on molecular filters. These filters are dissolved in an ethanol-ethyl acetate solution and the zinc sulfide content measured by electronic counting of the phosphorescence.[1] After centrifuging, to eliminate interference from zinc sulfide or dust particles and alcoholic KOH addition, the fluorescein content was determined from the solution fluorescence utilizing a spectrofluorometer.

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* Membrane filter No. AM-1, Gelman Instrument Co., Chelsen, Michigan.

The sensitivity of these measurements allow the detection of less than 5×10^{-9} grams and cross contamination of greater than 10^4 times the tracer being investigated can be tolerated. The remarkable lack of cross interference and the simplicity of the technique makes it ideal for large air mass sampling.

EXPERIMENTAL

The quantitative determination of zinc sulfide on molecular filters by phosphorescence requires solution of the filter without affecting the zinc sulfide crystal.[1] In addition, a simple rapid technique was needed to estimate the fluorescein present in this solution, since thousands of samples would be involved in field experimentation. It was necessary to determine the response of the instrumentation to fluorescein and to redetermine the zinc sulfide response, since improvements had been made to extend the sensitivity of the counting equipment. The cross interference measurements and the effect of the presence of zinc sulfide and fluorescein on each other were essential to the sensitivity and value of the method.

Mass Calibration of Zinc Sulfide

Standard slurries of zinc sulfide were prepared from weighed quantities of zinc sulfide carried in the solvent used to dissolve the molecular filters (the solvent was prepared by mixing 25 per cent ethanol with 75 per cent ethyl acetate and then dissolving one molecular filter for each 8 ml of solvent in order to similate actual field sample techniques). This solution will hereafter be known as filter solvent.

The samples, contained in 8-ml vials, were exposed to a moderate flux of 3650 A light (Circline fluorescent lamp). They were then automatically removed into the dark counting chamber and counted in a standard liquid scintillation spectrometer* after a constant delay of 6 seconds. Figure 1 illustrates the instrumental response to zinc sulfide phosphorescence.

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* Packard Instrument Co., LaGrange, Illinois.

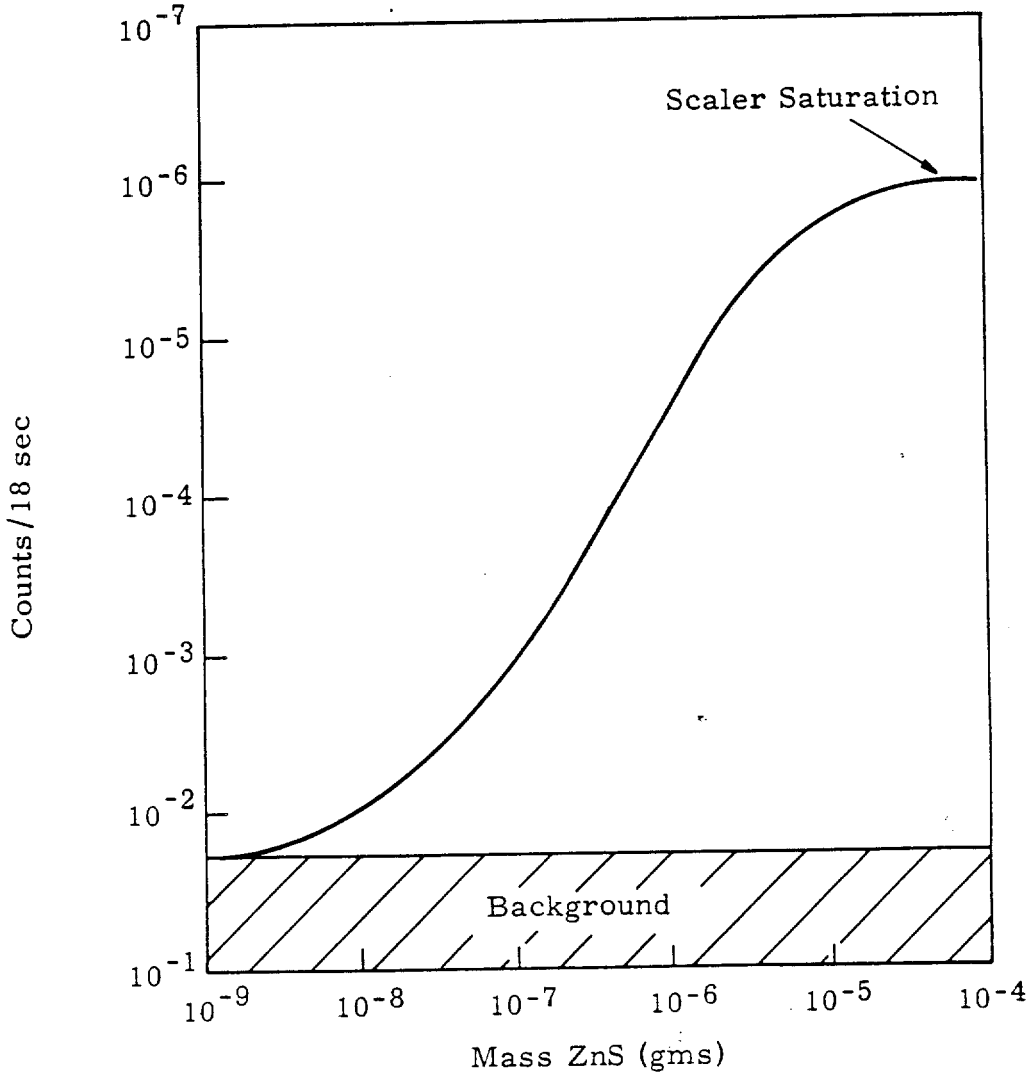

FIGURE 1

Calibration of Liquid Scintillation Spectrometer
Vs ZnS Concentration

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Mass Calibration of Fluorescein

The fluorescence emission from fluorescein was measured in a spectrofluorometer.* Standard solutions of fluorescein were prepared by dissolving weighed quantities of fluorescein in the ethanol-ethyl acetate solvent. Dilutions were made with the same solvent to encompass the required concentrations. Care must be taken to prevent excessive evaporation of the solvent while calibrating sample dilutions. Fluorescein is only slightly soluble in the ethanol-ethyl acetate, and no more than about one milligram can be expected to dissolve in an 8-ml volume.

The spectrofluorometer is designed to accommodate 3-ml volume cuvettes and detect fluorescent light in the same plane at a 90-degree angle to excitation light. The excitation monochromator was set at about 490 mμ and the analyzing monochromator set at 540 mμ. In order to improve sensitivity, a maximum light flux was accommodated using the large, 20 millimicron, entrance-exit slits. A consideration of the absorbance and fluorescence spectra of fluorescein will reveal the close proximity of their maxima (488 mμ versus 533 mμ) and overlap of their general spectra. It was thus necessary, to prevent excessive detection of scattered excitation light, to select excitation light of shorter wave length than the maximum and detect fluorescence at a longer wave length than the fluorescein peak. The light detector was the best (gain versus noise) of twelve 1P21 multiplier phototubes.

Fluorescein was found to have its fluorescence seriously reduced in the solution necessary to dissolve the molecular filters. This was believed to be the result of alcohol hydrolysis products of ethyl acetate shifting the fluorescein dye to the leuco form. Fluorescence may also be expected to vary considerably with solvent, due to nonradiative molecular interactions or gross solvent interaction, and further by differences in degree of ionization and H-bonding characteristics.

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* Cat. No. 104242, Farrand Optical Co., Inc., New York.

It was found that the addition of 8 drops of 0.05M alcoholic KOH to the 3-ml sample shifted the equilibrium sufficiently and contributed to more colored resonance forms of the dye. Although the solvent does not contribute measurably to fluorescence in the fluorescein spectral region, significant fluorescence was observed from the dissolved molecular filter. If the KOH concentration is raised to 0.5M, the filters' fluorescence is equivalent to 10^{-8} grams of fluorescein. This would reduce the sensitivity of the technique, consequently pH control is necessary. The results of fluorescein calibration measurements (background subtracted) with and without KOH addition are shown in Figure 2. It can be seen that the fluorescence is linear over several orders of magnitude of dye concentration (10^{-9} - 10^{-5} grams). The fluorescence then goes through a maximum and decreases thereafter. This is the result of several factors including concentration quenching, absorbance-fluorescence spectral overlap, dimer formation, and a limited light flux (10^{16} per second) compared to the molecules available for excitation.

Cross Interference Measurements

Samples of fluorescein in filter-solvent were prepared in 8-ml glass vials. These were exposed to light in the same manner as zinc sulfide samples and then counted in the normal manner after a 6-second delay. Although not noted for exhibiting phosphorescence, it is interesting that fluorescein does, indeed, contribute to delayed emission. Fortunately, however, the amount of phosphorescence due to the dye can be neglected for samples having less than 10^{-4} grams of fluorescein. More specific information concerning the afterglow of fluorescein is exhibited in Figure 3. It should be noted that the phosphorescence from about 10^{-4} grams of fluorescein corresponds to only 2.2×10^{-8} grams of zinc sulfide.

The zinc sulfide pigment used in these experiments for atmospheric dispersion studies emits light which has its maximum at about 540 mμ,

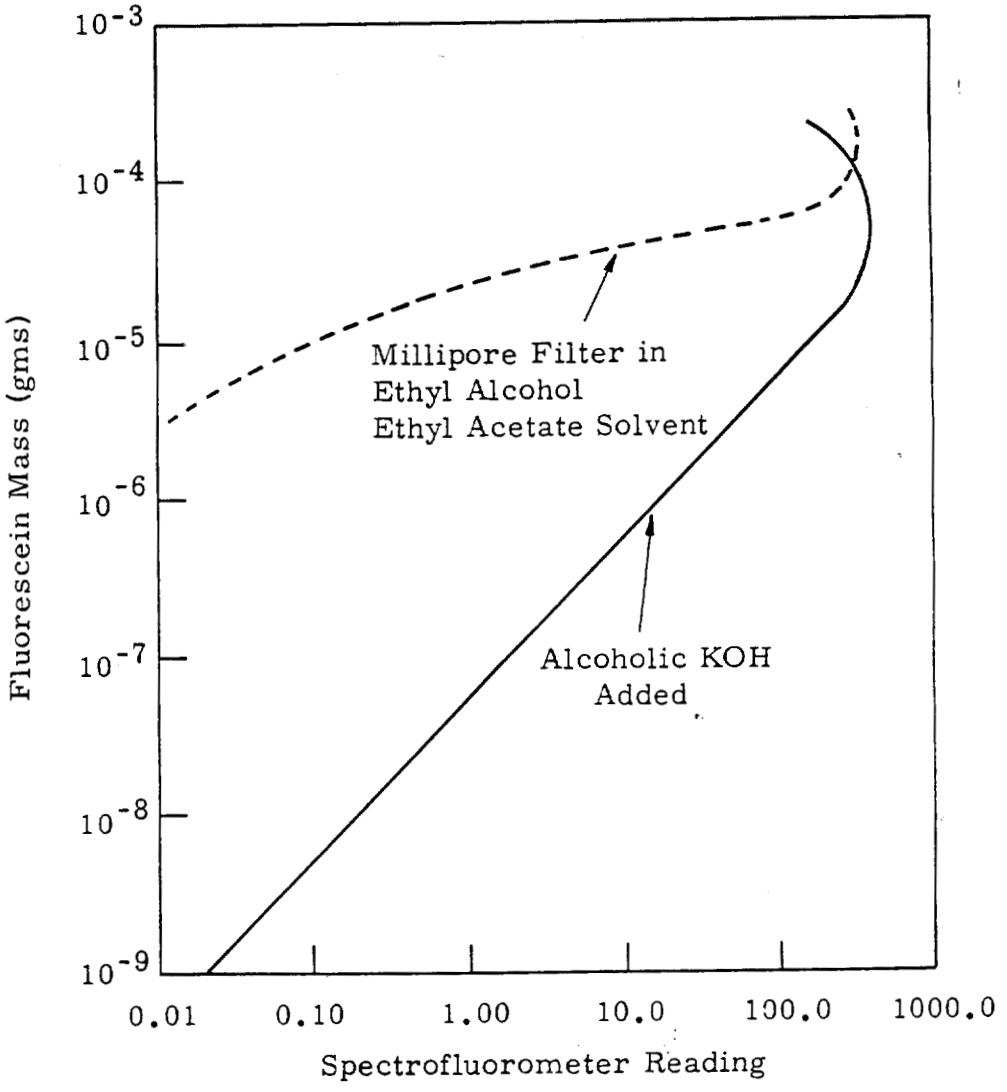

FIGURE 2

Calibration of Spectrofluorometer
Vs Fluorescein Concentration

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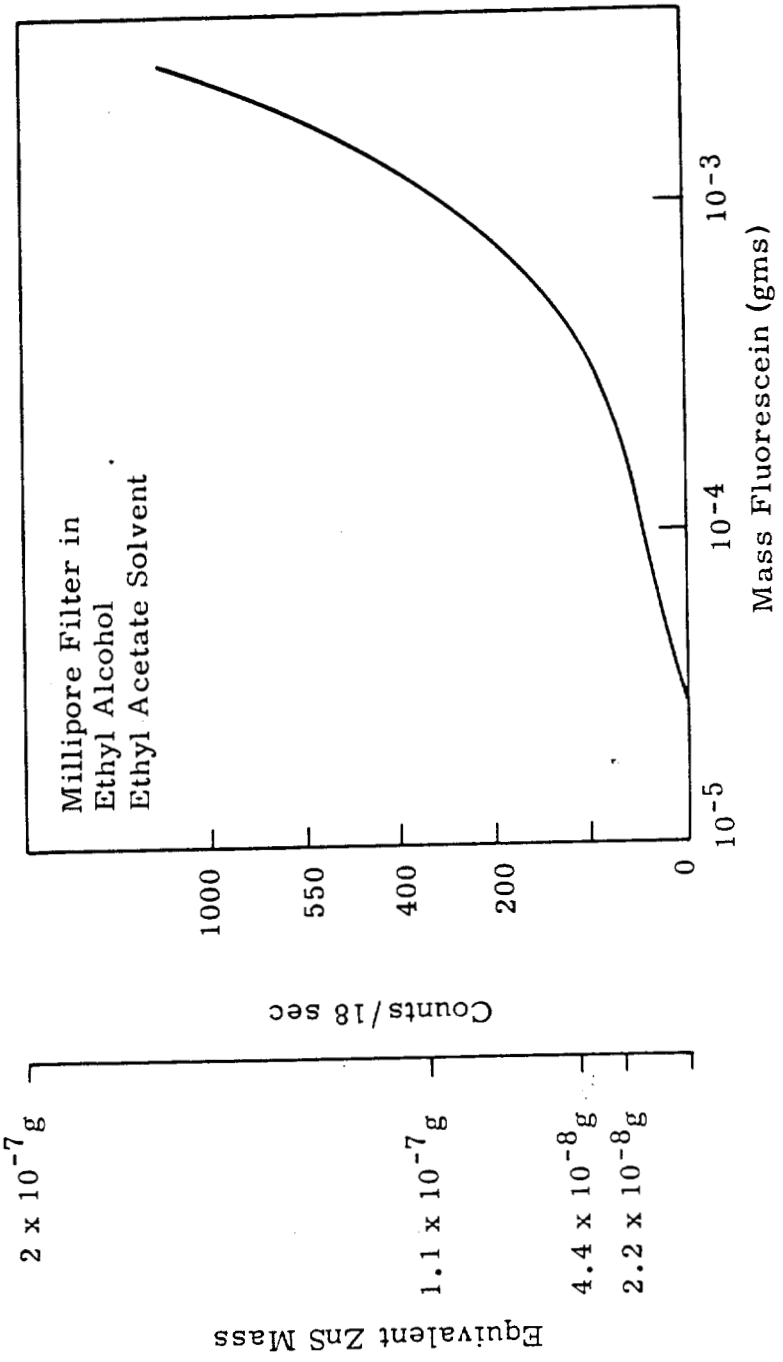

FIGURE 3

Phosphorescence of Fluorescein

while the fluorescein absorbs rather readily in this region. In order to determine the effect on the efficiency of zinc sulfide counting due to fluorescein, samples of zinc sulfide were spiked with varying amounts of fluorescein. Several fluorescein dilutions were prepared in the ethanol-ethyl acetate solvent and added to samples containing from 2×10^{-8} to 6×10^{-6} grams of zinc sulfide. This corresponds to counting rates from 140 to 400,000 in the 18-second interval used when determining zinc sulfide quantitatively. Figure 4 illustrates the reduction of zinc sulfide counting efficiency with increasing fluorescein concentration. The curve is actually a combination of fluorescein phosphorescence minus the loss in efficiency due to color, with the efficiency reduction being the dominant factor in all but trace zinc sulfide concentrations. It should be noted that at higher concentrations of fluorescein, there is no additional loss in counting efficiency. This is due to the fluorescein saturation of the solvent rather than to other physical phenomena.

When samples of zinc sulfide containing fluorescein impurity were allowed to stand overnight, reduction of the dye color occurred. The net result was to improve the zinc sulfide counting efficiency; however, this technique is not recommended since the dye color varies with the amount of incident light exposure. Reproducible zinc sulfide results were obtained when the samples were counted anytime from 20 minutes to 3 hours after filter dissolution. Most samples will contain less than 10^{-5} grams of fluorescein, thus the efficiency effect is negligible.

As mentioned earlier, the spectral emission (fluorescence and phosphorescence) from the zinc sulfide used has its maximum in close proximity with both the absorbance and fluorescence of fluorescein. Interference would then be expected from zinc sulfide when fluorescence measurements on the spectrofluorometer were taken. In order to determine this quantity, samples of zinc sulfide in filter solvent were prepared in the quartz cuvette and the fluorescence measured. The response of the

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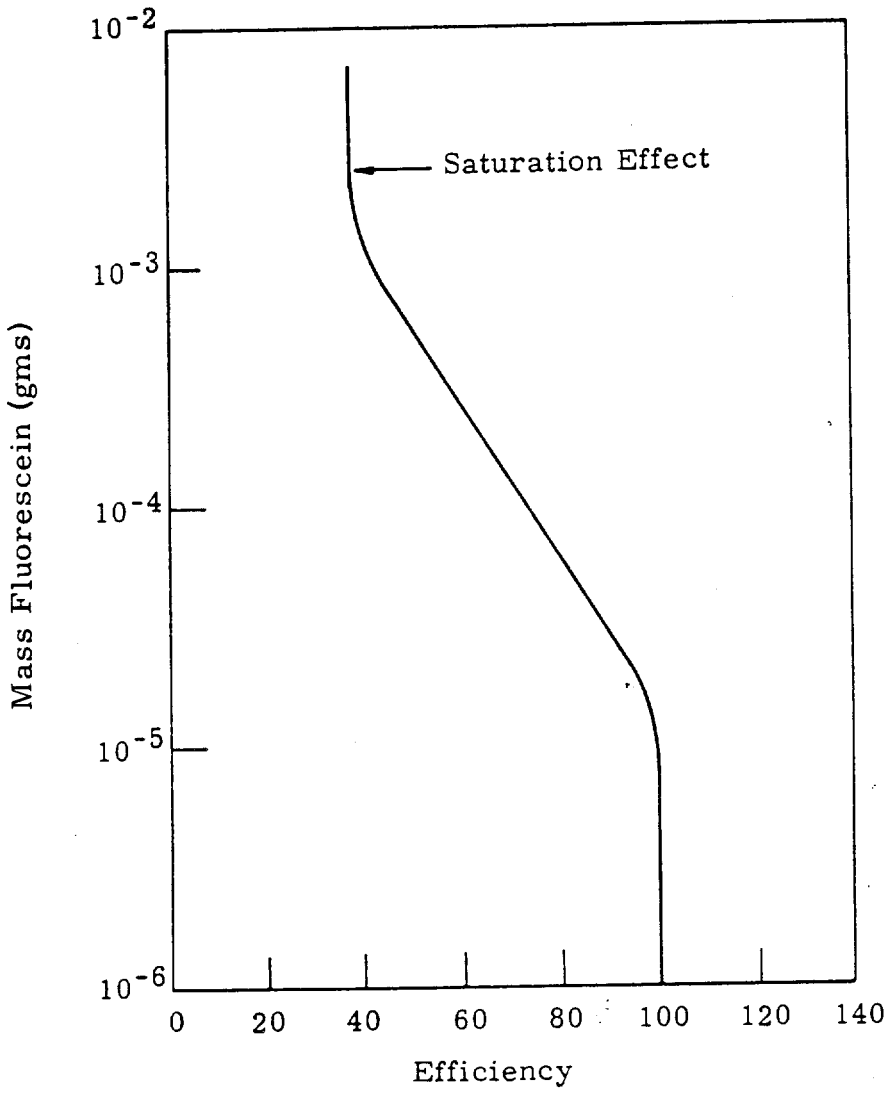

FIGURE 4

Loss of ZnS Counting Efficiency Due to Fluorescein

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spectrofluorometer to zinc sulfide fluorescence is illustrated in Figure 5. Also included in the graph is the equivalent fluorescein mass for a given zinc sulfide quantity. Zinc sulfide interference can be entirely eliminated if the sample is first centrifuged before an aliquot is taken for fluorescence analysis. This technique is recommended for field samples, since it also eliminated the other airborne contaminants, which may contribute up to 1 gram of dirt per sample.

It was observed and mentioned in zinc sulfide efficiency attenuation measurements, that the color or fluorescence of fluorescein diminishes with time. Although the zinc sulfide measurement can easily be carried out quickly after filter dissolution, the same may not be true for fluorescein determination. The effect of time on samples whose fluorescence is to be measured is of particular importance. A batch of filter solvent was prepared, divided in half, and fluorescein added to one half so that 3 ml would contain 2.7×10^{-8} grams. The fluorescence of these solutions was followed with time. Results of this experiment as well as the stability of the spectrofluorometer are indicated in Table I. It is apparent that fluorescence is reproducible when the alcoholic KOH is added just before measurement.

TABLE I

EFFECT OF TIME ON FLUORESCENCE MEASUREMENTS

Time	Fluorescein Sample	Spectrofluorometer Reading	Alcoholic KOH Reading
1330	Blank	.081	.081
	2.7×10^{-8} g	.080	.60
1335	Blank	.080	.086
	2.7×10^{-8} g	.082	.60
1505	Blank	.075	.078
	2.7×10^{-8} g	.072	.56
1605	Blank	.086	.086
	2.7×10^{-8} g	.082	.64
0955	Blank	.070	.080
	2.7×10^{-8} g	.071	.61

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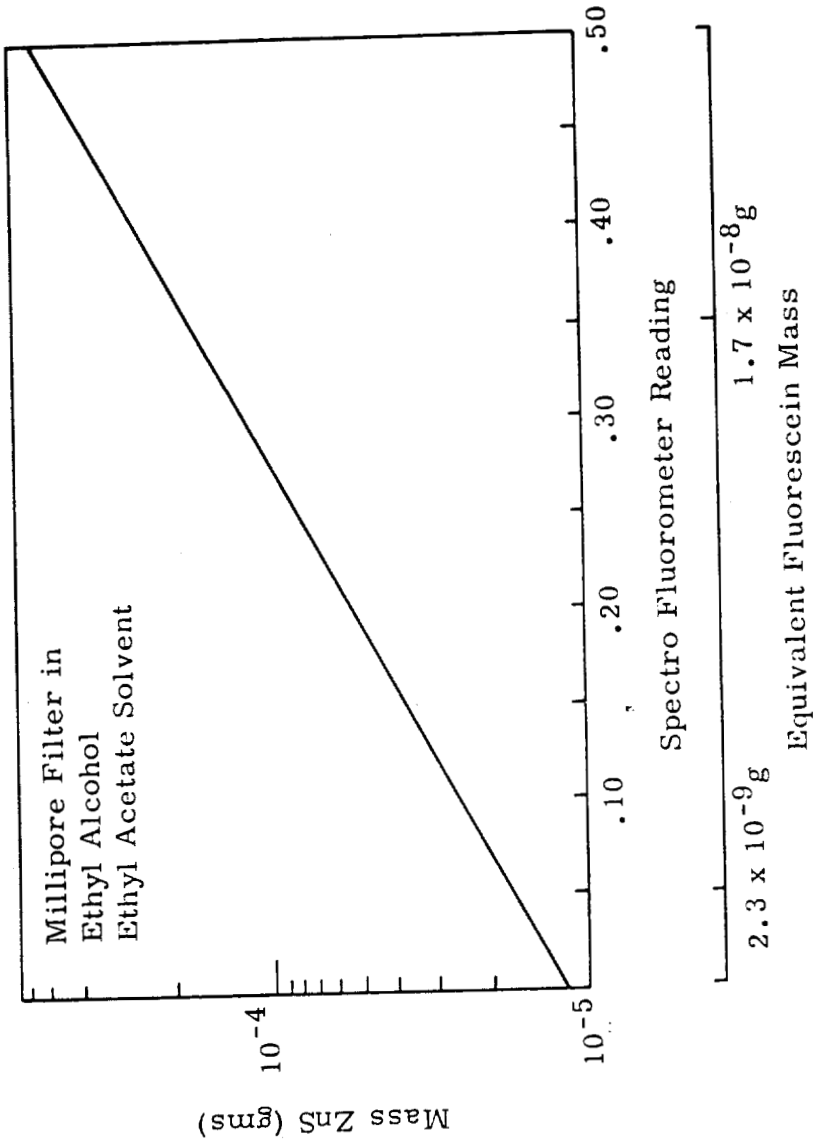

FIGURE 5

Fluorescence of ZnS in the Spectrofluorometer

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Experimental Summary

Analysis of zinc sulfide and fluorescein was carried out in the following sequence:

1. The molecular collection filter was placed in an 8-ml vial and dissolved in the ethanol-ethyl acetate solvent.
2. Zinc sulfide phosphorescence was then determined by counting in a liquid scintillation spectrometer and the dust content determined in a colorimeter.
3. The vial was centrifuged and a 3-ml aliquot placed in the spectrofluorometer cuvette.
4. The solution was stirred after addition of 8 drops of 0.05M KOH and the fluorescence read.

DISCUSSION

This study was undertaken in order to develop a method for analysis of two tracers after simultaneous dispersion to the atmosphere. An analytical method was developed for quantitative determination of fluorescein in the presence of zinc sulfide.

The remarkable lack of cross interference of fluorescein in measuring zinc sulfide by phosphorescence and of zinc sulfide in measuring fluorescein by fluorescence enables one to measure both throughout a wide range of filter loadings.

It is probable that the detection sensitivity of 1×10^{-9} grams for fluorescein could be improved by about a factor of 10 providing the experimental method was modified to incorporate aqueous leaching of the dye from the filter before dissolution. This procedure was attempted; however, the added time involved for sample analysis would be prohibitive in a large air sampling program. The simple, rapid technique for fluorescein detection subsequent to zinc sulfide counting allows a reasonable time for the

combined analysis. No effort was extended to reduce solution quenching agents, such as dissolved oxygen, since their contribution was apparently small.

The technique of dual tracer analysis will be field tested at the Hanford Meteorological site where work on the zinc sulfide dispersion measurements have been going on for some time. Methods of fluorescein dispersal will also be developed.

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