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Table II. Relative Emission Intensity of Nickel

Stock solution. Nickel naphthenate (spectrographically pure dissolved in benzene) (500 p.p.m. Ni)
Solvent solution. 10% stock solution–90% other solvent

Solvent	Feed Rate, G./Min.	Relative Intensity, Ni 3414A. (Corrected for Feed Rate)
Acetone	1.86	18.3
n-Heptane	1.41	18.5
Methanol	1.28	18.6
Methylcyclopentane	1.60	14.0
n-Hexyl ether	0.46	19.5
Nitrobenzene	0.54	30.0
Toluene	1.87	16
Ethyl octane	1.50	19
Cyclohexane	1.13	25
Acetylacetone	1.10	20
Ethyl chloride	1.40	17
Monochlorobenzene	1.60	14
Xylene	1.70	17
Chlorobenzene	1.0	27
Methyl ethyl ketone	1.7	16
Benzene	1.8	19
Carbon tetrachloride	1.6	14
Ethanol	0.8	19

and then decreases rapidly as feed rate is further increased. This is attributed to a fall off in flame temperature at increased flow rates. Similar results were obtained in our laboratories. It is also probable that, at high feed rates, the energy liberated by the flame per unit weight of sample is low. Much of it may be used in evaporating the solvent instead of exciting the metal atoms. This would cause a profound decrease in emission intensity. However, it is apparent that careful control over feed rate is essential. The feed rates used in this work, shown in Table I, were measured directly by weighing the sample and container before and after aspiration for a known period of time.

The optimum feed rate found was approximately ten times as great as that reported previously. This may be due to differences in burner design.

Solvents. As can be seen from Table I, organic solvents in many cases enhance the intensity of emission for a given metal when introduced into the flame. It was observed that different organic solvents affect the intensity of the emission differently. This is illustrated in Table II, which gives the relative emission intensity exhibited by nickel in different solvents.

If flame temperature alone controlled the intensity of emission, all organic solvents would give similar enhancement effects. Since this is not the case, it seems that the efficiency of producing the emitting species is at least as important as the flame temperature (3). Physical properties of the solvent which can cause a change in emission include stability in the flame, the ease of combustion and liberation of the excited metal atoms, drop size, and ease of evaporation. No doubt some of the variation in the intensity of signal between different organic solvents can be explained by variation in aspiration rates for a given flame condition.

ACKNOWLEDGMENT

The author thanks the Humble Oil & Refining Co. for permission to publish this work and S. A. Bartkiewicz, who designed the burner used.

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Liquid Scintillation Techniques Applied to Counting Phosphorescence Emission

REPOSITORY PNL
COLLECTION Atmospheric Releases
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FOLDER N/A

Measurement of Trace Quantities of Zinc Sulfide

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▶ An analytical procedure is based on electronically counting the individual phosphorescence photons following light-excitation for the measurement of scintillation grade zinc sulfide particles on molecular air filters. The zinc sulfide was collected on these filters during meteorological studies of particle dispersion. The analytical procedure involves dissolving a zinc sulfide laden filter in an ethyl alcohol–ethyl acetate solvent, exposing the sample to a fluorescent lamp, allowing the sample to decay (in the dark) for a predetermined time, then counting the phosphorescence photon emission. The counting equipment requirements are similar to those commonly used for counting tritium. The conditions of excitation and measurement yielded a sensitivity of about 10^{-8} gram. A sensitivity improvement of one to two orders of magnitude could probably be obtained by minor procedural changes. The precision of the zinc sulfide measurements on clean and dirty filters is about ±3% and ±6% standard deviation. Corrections for loss in counting efficiency on dirty filters are made from absorbance measurements with a colorimeter.

Zinc sulfide powder (fluorescent pigment, No. 2210, U. S. Radium Corp., Morristown, N. J.) is used as a tracer in studying down-wind particle concentrations under different meteorological conditions. An aerosol generator discharged the finely divided material into the atmosphere, and collectors, using molecular filters (Membrane filter No. AM-1, Gelman Instrument Co., Chelsen, Mich.), are spaced around the generator for sampling.

The ZnS is commonly measured by visual counting techniques under ultraviolet light; however, recently an instrument was designed (8) using alpha excitation for its measurement. Although this instrument appeared to be satisfactory for measurements of "clean" filters (6), it was not capable of measuring ZnS in the presence of dust, soot,

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sand, or other air-borne dirt which is frequently collected along with the ZnS. Visual counting techniques were also unsatisfactory when the filter contained dirt.

In an investigation of possible alternate methods of analysis, it was observed that the phosphorescence component of light-excited ZnS was of sufficient intensity and duration to provide a very sensitive indication of its presence. Utilizing this property of ZnS, analytical procedures were developed for its measurement in trace amounts (as low as 10^{-8} gram) on both clean and dirty filters. Initially, a procedure was developed which required manual control of timing and sample positioning for the ZnS measurement. The procedure was subsequently modified for automatic operation to facilitate a large air sampling program.

This study was performed to demonstrate the practicability and potential sensitivity of this new technique without making a major effort to obtain the ultimate sensitivity of the method.

THEORETICAL

The results of the absorption of a quantum of radiation by molecules and crystals, particularly zinc sulfide, have been adequately summarized by a number of workers (*2, 7*). Absorption of a light photon by zinc sulfide results in the transition from a stable ground state to an excited state or conduction band. The energy difference between these levels is of the order of a few electron volts. There are several paths open to the excited molecules in addition to nonradiative transfer processes; two of these result in the emission of light photons. They may immediately (in 10^{-8} to 10^{-6} second) re-emit photons of either the same or a lower frequency; this emission is called fluorescence. Emission of photons may also take place more slowly by phosphorescence.

In the inorganic crystal, variations due to lattice defects or impurity centers occur which produce electronic energy bands in the normally forbidden region below the conduction band. The absorption edge for excitation of zinc-activated zinc sulfide is about 3350 A. while the inclusion of manganese impurity results in a shift to 3660 A. Electrons that have been raised to the conduction band by excitation may then enter an empty impurity level in their vicinity. These levels provide the mechanism by which transitions to the ground state result in light emission or fluorescence. The de-excitation path of concern in this study is a consequence of the so-called trap mechanism. This mechanism concerns levels from which transitions to the ground state are forbidden. As a result, electrons must return to the conduction band before de-excitation. This delay mechanism for light emission produces an afterglow called phosphorescence.

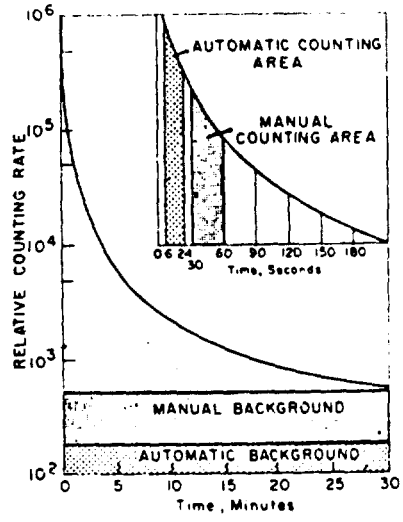

Figure 1. Zinc sulfide phosphorescence decay

The decay of the zinc sulfide phosphorescence is illustrated in Figure 1. These results were obtained after a 2-minute irradiation at about 14 inches from a 60-watt fluorescent lamp. The decay of the phosphorescence is relatively rapid, and the greatest sensitivity for its measurement is within the first minute of decay. In the manual unit, a finite time of about 20 seconds for sample transfer from irradiation to counting necessitated a delay of 30 seconds before measurement of the emitted light. An immediate 30-second count of the phosphorescence after the 30 second delay provides a very high sensitivity for the measurement. A background sample containing no zinc sulfide was unexcited and constant after similar treatment over the time interval measured. With the automatic unit, samples were delivered from the irradiation position to the counting position in 6 seconds, and the required sensitivity was obtained after an immediate 18-second count.

A study of the phosphorescence intensity as a function of irradiation time showed essentially no increase in intensity with irradiation times longer than a few seconds. In practice, an irradiation time of 2 minutes was used with the manually operated unit, since samples could not be handled at a much faster rate. With automatic operation a 5-second exposure was used, since the glass vial sample containers were found to exhibit short-lived phosphorescence in the 6- to 18-second counting region which increased with extended exposure.

The observed phosphorescence is due to the emission of single light photons from the excited crystal. In their detection with a multiplier phototube, a photon can, at best, produce one photoelectron at the photocathode. Actually, the quantum efficiency of the photocathode is only about 10%, thus, about one out of ten of the phosphorescence photons which strike the photocathode will release a photoelectron.

The pulse height spectrum obtained from the multiplier phototube would thus be the result of the amplification of single photoelectrons in lower mass samples and should be almost identical to that obtained from tritium, with a

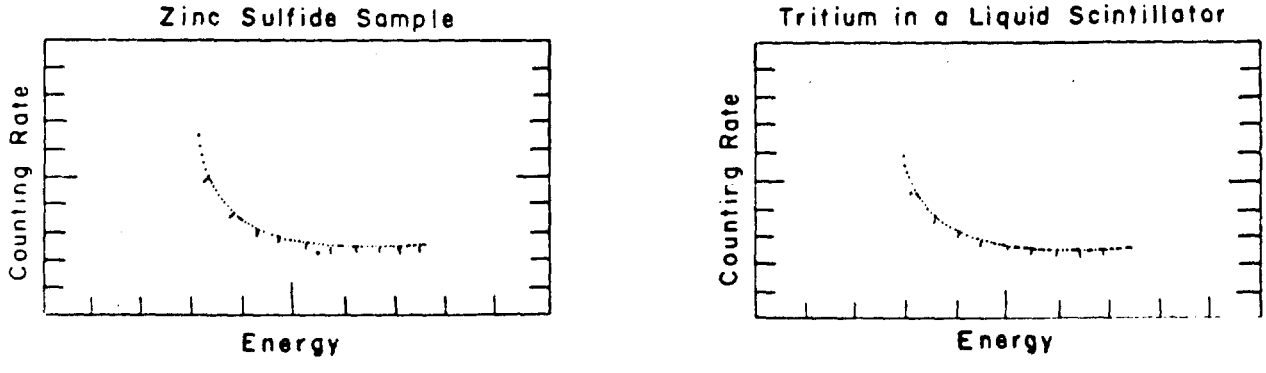

Figure 2. Comparison of spectra of zinc sulfide and tritium

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relatively inefficient liquid scintillator. (Even in an efficient liquid scintillation solution, tritium produces only a few photoelectrons per disintegration.)

The multiplier phototube output spectrum from zinc sulfide, after amplification, was measured with a multichannel analyzer, and it is compared with the spectrum of tritium, from an aqueous adaptable liquid scintillator (about 2% counting efficiency), in Figure 2. In this scintillator, since the average energy per disintegration is about 5 k.e.v., a large proportion of events will give only one or two photoelectrons from the tube cathode (*9*). It is apparent from these curves that the spectra are very similar. By a careful study of these data, using a method for the examination of spectra resulting from single photoelectron emission (*1, 5*), it was possible to establish that the spectra represented identical energy distributions and that they were both the result of comparable photoelectron emission from the photocathode. The instrumental requirements for measuring zinc sulfide are thus similar to those used for counting tritium by liquid scintillation techniques.

Zinc sulfide may be detected using alpha, beta, or gamma radioactivity for excitation and a phototube for detection of the immediate light fluorescence. This approach is not attractive, since the amounts of radioactivity required to produce a fluorescence comparable to the phosphorescence which follows light excitation cannot be handled conveniently. Also, the measurement of phosphorescence, following light excitation, critically limits interference, even from impurities which fluoresce.

INSTRUMENTATION AND EQUIPMENT

Manual Unit. The instrument used for counting the samples was a standard liquid scintillation spectrometer (Tri-Carb Model 314, Packard Instrument Co., LaGrange, Ill.). The detector system was contained in a deepfreeze and maintained at approximately 0° C. to minimize tube noise. For counting, the 2-dram vial sample containers were placed vertically in a 1¾-inch deep by ¾-inch diameter well of a 2-inch diameter by 2-inch long Lucite light pipe (*3*). The light pipe was viewed at each end by 2-inch Dumont 6292 multiplier phototubes in the conventional arrangement for coincidence counting. (In actual counting, the coincidence feature was not used since single photon events were being measured; therefore, the signal from only one tube was measured.) A magnetic stirrer was centered directly under the well of the light pipe to permit stirring during the measurements. Mineral oil (Scintillation Counter Mineral Oil, General Electric Cat. 9776095P1) was used as a light coupling agent between the well surface and vial.

Figure 3. Automatic counting equipment

The deepfreeze was enclosed in a "Black Room" made of 2 layers of velveteen originally designed to prevent phototube excitation while sample changing. This arrangement was particularly useful in preventing re-exposure of samples during their transfer to the counter.

The apparatus for light excitation consisted of 60 watts of fluorescent lamps placed approximately 14 inches above a magnetic stirrer. The sample was centered in a vertical position in a small black box on the stirrer. The box was fitted with a lid which could be closed in about 0.1 second to permit reasonably accurate timing between excitation and counting. Prior to the light excitation, the samples were placed on a mechanical shaker for 2 minutes to further ensure even dispersion of the ZnS and dirt in the samples.

Automatic Unit. A standard Model 314 X Tri-Carb liquid scintillation spectrometer was modified in the following manner to detect ZnS phosphorescence. The automatic shield was changed to accommodate 2-dram vials, a load-unload switch added to replace the automatic sample changing mechanism, and a second high speed transistorized scaler added in the tens unit to accommodate the extremely high counting rate observed in some samples after the 6-second delay period.

Essentially, the same techniques were used for sample preparation and counting as in the manual operation; however, an optical coupling between sample and photocathode was not used in the automatic operation. The light excitation and counting equipment is illustrated in Figure 3.

A Klett - Summerson colorimeter, which was modified to accept the 2-dram vials, was used without filter to measure the relative absorbance of the samples.

EXPERIMENTAL

The application of this new counting technique required a solvent for the filters which would not phosphoresce, quench the phosphorescence of the ZnS, or dissolve the ZnS. A means of holding the ZnS in a reasonably uniform suspension in this solvent during its excitation and counting was required. It was essential to determine the response of the counters to the mass of ZnS present to establish a ZnS mass to counting-rate calibration and to determine the reproducibility of the measurements. The ZnS had to be measured in the presence of zero to about 1 gram of air-borne dirt; therefore, it was necessary to know the counting efficiency of the ZnS in slurries containing various amounts of dirt and to determine if this dirt exhibited any phosphorescence.

Selection of Filter Solvent. Previous work on liquid scintillation counting by one of the authors (*4*) had shown that a mixture of 25% ethyl alcohol 75% ethyl acetate was an excellent solvent for ester-type filters, and also that neither scintillations nor light quenching would occur in the mixture. Counting rate measurements on blank filters in this solvent, under the conditions being studied for this procedure showed that essentially no phosphorescence photons were emitted by the solvent or filter (see Figure 1). It thus appeared that the ethyl alcohol-ethyl acetate was an ideal liquid for suspending the ZnS during its measurement, as well as being a good solvent for the ester filters; therefore, no other solvent systems were investigated.

The fact that this solvent was well suited for this was further verified by the observation that the counting efficiency of standard samples of ZnS, which were prepared at the onset of this study, did not change perceptibly during a 2-week period.

RESPONSE AND MASS CALIBRATION

Manual Operation. As described under Instrumentation and Equipment, 2-dram glass vials (approximately 8.5 ml.) were used as sample containers. To determine the response of the counter as a function of the ZnS weight in these samples standard slurries of ZnS were prepared in the following manner. Approxi-

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mately 1 mg. of ZnS was accurately weighed in a weighing bottle on a microbalance. Ten milliliters of solvent (25% ethyl alcohol-75% ethyl acetate at 0° C.) and a magnetic stirring bar were added, and the mixture was then placed in an ice bath on a magnetic stirrer. The low temperature prevented evaporation loss during the subsequent pipetting operations, and vigorous stirring maintained a uniform suspension. Dilutions of the original slurry were prepared by pipetting aliquots into 10- to 20-ml. volumes of the solvent which were cooled and stirred as described above. Experience in pipetting these slurries showed that they could be pipetted with reasonable accuracy if pipets (400 or 500 λ) were used, and if they were rinsed well both in parent and daughter slurries. (The pipet was filled several times, discharging the contents back into the parent slurry before accepting a pipet full, then the pipet was rinsed several times with the daughter solution after discharging the aliquot into it.)

Aliquots of these standard slurries which contained 10^{-8} to 10^{-5} gram of ZnS were placed in the 2-dram vials along with a dissolved filter and a magnetic stirring bar. The vials were then filled to the neck with solvent and counted in the normal manner. The counting rate was directly proportional to the ZnS mass in the sample. The response of the instrument was thus demonstrated to be linear.

To obtain a ZnS mass to counting-rate calibration, and at the same time ensure the maximum accuracy in dilution and pipetting, standard sample preparation was carried out in the following manner.

A 989-μg. sample of ZnS was weighed in a weighing bottle on a microbalance. This sample was slurried in 10 ml. of solvent, as discussed previously, and three dilutions of the slurry were prepared by transferring 500-λ aliquots to 10-ml. portions of the solvent. Two or three 500-λ aliquots of each daughter slurry were placed in 2-dram vials with a dissolved filter and a magnetic stirring bar. The observed counts from these standards are presented in Table I.

In addition to providing the required information for the mass calibration, the data in Table I also illustrate the precision which can be obtained in pipetting and diluting these slurries.

Automatic Operation. Continual magnetic stirring during light exposure and counting was unnecessary when the process could be completed within 30 seconds after shaking. This instrument was calibrated using samples which contained 10^{-8} to 10^{-4} gram of ZnS (Figure 4). High counting rate samples containing more than 5×10^{-6} gram of ZnS required time delays before determination. The instrument was designed to automatically repeat operation, after a count-printout cycle, thus incorporating delay periods amounting to 29 seconds. The number of periods used are listed beside the individual

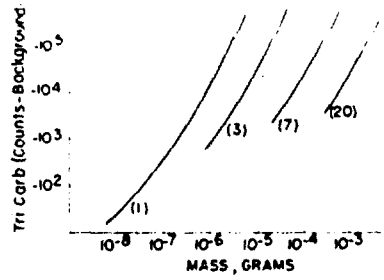

Figure 4. Mass calibration curve

curves in Figure 4. The instrument response was not linear, as was the case with the manual equipment, but was better described by the expression,

$$\log N = A + B(\log M) + C(\log M)^2 \quad (1)$$

where N is the counting rate and M is the mass. This response is not fully understood; however, it may be associated with the extremely high counting rates during the first few seconds of counting time (see Figure 1). Thus, a greater fraction of large or multiple pulses, whose detection efficiency varies as a power function, would now contribute to the total counting rate.

In Figure 4 the integral counts total 300,000 in 18 seconds with about 10^{-5} gram of ZnS. This is the maximum counting rate which could be accurately handled by the instrumentation. An upward extension of the calibration region could be accomplished through an amplification reduction which reduces the specific counting rate, or, as was found more desirable and is illustrated, through increase of the delay between exposure and counting.

Reproducibility of Measurements on Clean Filters. Six filters on which ZnS was collected during actual field tests were obtained and counted three times each to determine the reproducibility of the counter. The observed counting rates with their calculated standard deviations are included in Table II.

The average variation in counting for individual samples in the range of 10^{-7} to 10^{-5} gram is ±1.75%.

Measurement of Zinc Sulfide on Dirty Filters. The above samples were clean filters; no darkening from dust, soot, or dirt was apparent. Before attempting to measure the ZnS on dirty filters, it was necessary to determine if dirt exhibits any phosphorescence under the conditions of measurement. From measurements of dirty filters containing no ZnS and from measurements of blank samples which had dirt intentionally added, it was established that any phosphorescence from the dirt was negligible.

Since many of the samples collected during field tests contained a considerable amount of dirt, it was essential to devise a method for measureing the counting rate attenuation produced by various amounts of dirt on these filters. Direct and indirect methods of measuring this attenuation were studied and are described here. The direct method simply involves counting the sample, then spiking a known amount of ZnS into the sample and recounting to determine the attenuation of the added spike. The indirect method requires that a calibration curve be prepared to relate the counting efficiencies of the dirty samples as measured above to their absorbance as measured on a standard colorimeter with a white light source. A set of 20 field-collected dirty filter samples were obtained for these calibrations. They each contained some ZnS and various amounts of dirt in quantities up to approximately 1 gram. These samples were each counted twice to

Table I. Data for Zinc Sulfide Mass to Counting-Rate Calibration

(2.36 μg./sample)

Dilution No.	Aliquot No.	Observed Count
1	1	53,390
	2	53,158
2	1	53,127
	2	53,188
3	1	56,198
	2	52,130
	3	51,058

Av. count = 53,178
Std. dev. = ±2.95%
counts/μg. = 52,615/2.36 = 2.25×10^4

Table II. Reproducibility in Measurement of Zinc Sulfide on Field Test Filters

Sample Designation	First Count	Second Count	Third Count	Average	Per Cent Standard Deviation
A	122,591	118,192	123,203	121,329	0.22
B	12,128	13,192	12,536	12,622	4.25
C	3,518	3,384	3,517	3,473	2.22
D	6,750	6,606	6,773	6,710	1.35
E	28,871	30,971	31,690	30,511	1.52
F	58,581	55,998	55,564	56,714	0.909
				Av. std. dev.	= 1.75

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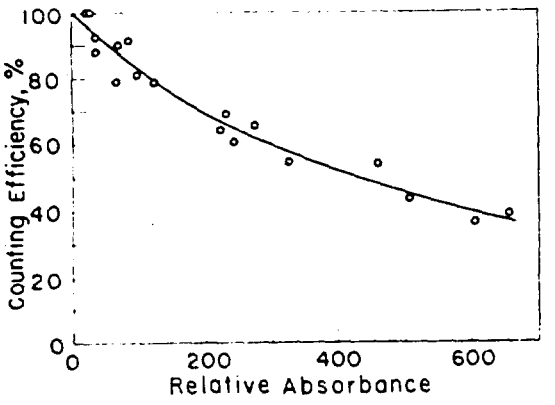

Figure 5. Effect of air-borne dirt on counting efficiency of zinc sulfide

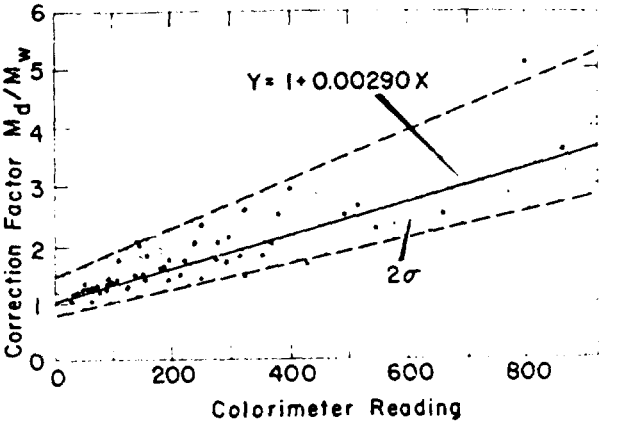

Figure 6. Correction factor for air-borne dirt on zinc sulfide counting efficiency

determine the reproducibility of counting dirty filters, and were then spiked with a known amount of ZnS and recounted to determine their counting efficiency. Without removing the samples from their 2-dram vials, they were shaken on a mechanical shaker to give fairly even distribution of the dirt and ZnS, and their absorbance to white light was measured with a Klett-Summerson colorimeter.

The duplicate counts of these dirty filter samples, along with their standard deviations, are included in Table III. Also included are their counting efficiencies relative to clean filters (as measured by spiking with ZnS), and their absorbance as measured by the colorimeter. The variations in repetitive counting of dirty filters are greater than those observed on the clean filters (see Table II).

To better illustrate the relationship between the counting efficiencies of the dirty filters as measured by the spiking technique and the absorbance of the samples, these values have been plotted and are shown in Figure 5.

One other technique was used to eliminate pipetting error in spiking. Clean filters with various amounts of ZnS were counted and subsequently recounted after the addition of a dirty filter. The reduction in original count demonstrated the efficiency for detection, and a colorimeter reading indicated the turbidity. Results of this method are plotted on Figure 6, where M_D/M_W is the correction factor greater than one, applied to the experimental mass to compensate for dirt interference. In both cases, a rather good relationship exists between counting efficiency and absorbance, and an absorbance measurement of each sample provides a good estimate of the sample's counting efficiency. These techniques eliminate the need for spiking and recounting each dirty sample.

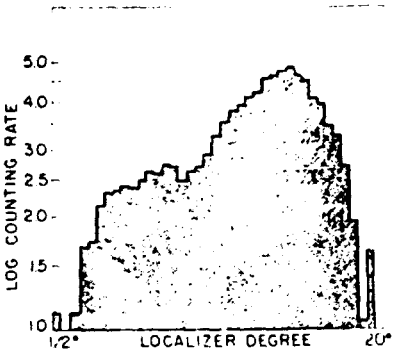

Figure 7. Zinc sulfide wind flow pattern

Table III. Reproducibility of Dirty Filter Counting Measurements and Comparison of Their Counting Efficiencies with their Absorbance

Sample No.	Count 1	Count 2	Added Spike Counts	(ZnS Spiking) Counting Efficiency	Relative Absorbance[a]
1	38,016	37,489	42,590	100.0	24.5
2	1026	1169	42,310	99.7	23.5
3	1474	1715	39,115	92.2	40.0
4	15,701	16,386	37,386	88.1	36.0
5	46,653	46,038	33,339	78.6	66.0
6	9615	8979	38,538	90.8	85.0
7	1499	1472	40,116	94.5	69.0
8	2183	1896	34,304	80.8	96.0
9	5134	4674	29,269	69.0	233.0
10	10,517	10,386	27,255	64.2	222.0
11	1864	1762	33,336	78.5	124.0
12	2315	2388	25,615	60.1	241.0
13	1559	1709	27,743	65.4	274.0
14	1584	1275	26,995	63.6	240.0
15	1333	1143	22,699	53.5	458.0
16	742	739	23,064	54.3	325.0
17	337	397	18,467	45.5	505.0
18	1779	1535	15,349	36.1	605.0
19	1344	1281	16,489	38.8	655.0

Av. std. dev. of Count 1 and Count 2 = ±5.95%

[a] In meter units on Klett-Summerson colorimeter.

DISCUSSION

The purpose of this study was to develop a procedure of a specified accuracy and sensitivity for the measurement of ZnS particles on air filters. Since this objective was readily realized by this rather unique and new technique of measurement, no effort was made to obtain the maximum potential precision or sensitivity for the method.

In actual field test experimentation, air sampling stations (from 3 to 200 feet absolute elevation) are positioned in arcs at various distances from the dispersion point. The 2-mile downwind distribution pattern determined by ZnS analysis is illustrated in Figure 7. It is evident, from the quantities of ZnS present at the lateral sampling locations, that a highly sensitive detection system is necessary to accurately characterize wind patterns.

It is apparent from the preceding sections that a large increase in sensitivity could be obtained by certain improvements. First, the light source was simply fluorescent lights positioned

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about the sample. This light intensity at the sample, and the resulting phosphorescence of the samples, could probably be increased by an order of magnitude. Second, the optimum excitation frequency could be determined and a strong light source of this frequency used. This would, of course, increase excitation of the ZnS, but should also minimize excitation of the glass container or any dirt in the sample. Third, the phosphorescence emission varies considerably between types of ZnS pigment, and no attempt was made to select the pigment which would optimize sensitivity.

In addition to providing a new and unique method of analysis, this procedure has been used to calibrate the alpha excitation instruments (*8*) (which measure ZnS directly on clean filters) and to demonstrate that their response is linear on clean "field-run" filters.

This technique could be applied to the measurement of particle distribution (using ZnS as a tracer) on ground surfaces in different types of terrain and under different meteorological conditions, since ZnS can be measured in the presence of dirt. In a more general way, this technique could be applied to the measurement of any material which has a sufficiently high phosphorescence yield and a sufficiently long decay rate. It is approaching the ultimate in sensitivity, since the individual phosphorescence photons resulting from electronic excitation of single molecules are being counted. The technique could be further refined by using optical spectrometric techniques to separate the desired wave lengths prior to measurement.

ACKNOWLEDGMENT

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Absorption Spectra of the Lanthanides in Fused Lithium Chloride–Potassium Chloride Eutectic

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▶ Spectra are presented for solutions of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium fluorides in fused lithium chloride–potassium chloride eutectic at 400° C. These spectra are discussed and compared with similar results which have been obtained in the same and other fused salt media and in aqueous solutions. Molar absorptivities for selected absorption bands of the rare earth spectra which might be useful in quantitative analytical determinations are also given.

THE ABSORPTION SPECTRA of fused salts have been of interest for some time as aids in studying the chemical constitution and electronic structure of these media both as pure salts (*12, 14–17, 21*) and as solutes in fused salt solutions (*3, 5–9, 18, 19, 21–24, 26–28*). This investigation is concerned with the determination of the unique absorption spectra of dilute solutions of various lanthanide fluorides in fused LiCl–KCl eutectic solvent, and the determination of the molar absorptivities for significant absorption bands from these spectra.

The molar absorptivities of the bands of analytical interest are tabulated in the same form that Banks and Klingman (*2*) used for their results on aqueous solutions of rare earth mixtures. The absorbance of the solvents used was determined at the same temperatures and in the same quartz cells used for recording the spectra of the rare earth solutions, and then was subtracted from the absorbance of the solutions to obtain the absorption spectra of the solutes.

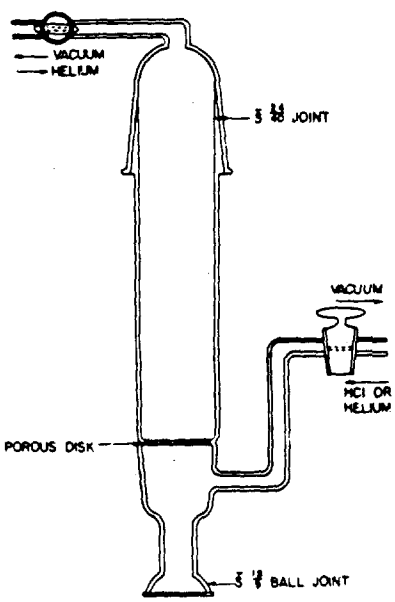

Figure 1. Eutectic purification and filtering apparatus

EXPERIMENTAL

Apparatus and Reagents. The spectra were obtained with a Cary Model 12 spectrophotometer using an electrically heated cell-block furnace as the cell holder. The high temperature cell assembly was similar to the one used by Sundheim and Greenberg (*22*). The temperature fluctuated ±0.5° C. in the cell block and less than ±0.1° C. in the fused salt solutions contained in the optical cells. The optical absorption cells used were one-piece quartz cells having 1-cm. light paths. These square cells were connected to a borosilicate glass ball joint by a graded seal. The ball joint could be connected to either an outer joint fitted with a vacuum stopcock for sealing the cell or to the outer joint of the filtering apparatus used in filling the cells with molten solutions. The graded seal and tubing between the cell and the ball joint provided the necessary capacity for the LiCl–KCl eutectic when it was loaded in the solid state. The lanthanide fluorides used were prepared at the Ames Laboratory of the Atomic Energy Commission and analyzed for fluoride and rare earth metal content.