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A Portable Fluorometric Monitor to Detect Polynuclear Aromatic Hydrocarbon Contamination of Work Area Surfaces

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MASTER

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DISCLAIMER

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ABSTRACT

A Hand-held fluorometric monitor for detection of surface contamination by polynuclear aromatic (PNA) compounds is described The instrument will indicate the presence of microgram quantities of PNA in the workplace at distances $\leq$ 1 m. Laboratory test data using coal liquefaction products and wastes are presented. It is anticipated that this type of "spotter" will be used extensively in monitoring for PNA contamination of the "clean" areas of coal conversion facilities, such as lunch rooms, shops, changing facilities, the control room, etc. Actual field evaluation of two spotter units at several coal conversion pilot plants is scheduled to begin during FY 1980.

I. Introduction

Uptake of polynuclear aromatic (PNA) compounds via contact with contaminated surfaces in the workplace has been identified as a major mode of worker exposure (1). Thus, the need for instrumentation to monitor PNA buildup on workplace surfaces as, for example, results from aerosol condensation, has also been recognized (1,2). Such instrumentation must be capable of: (a) functioning during actual plant operation in varied working environments; (b) detecting material spilled on different work surfaces, including machinery, plumbing, construction materials, and on personnel and clothing; and (c) being easily and reliably operated by all plant personnel.

The fluorescence spotter described in this paper (U.S. Patent applied for) has these capabilities. This instrument, which consists of a hand-held optics unit connected via an umbilical cable to an electronics module (Fig. 1), enables remote monitoring of work area surfaces at distances $\leq$ 1 m. The electronics module, which normally operates with AC power can also be operated on rechargeable batteries; thus the entire instrument plus battery pack is portable.

It is anticipated that portable fluorescence spotters will be used extensively to detect surface contamination in changing areas, lunch rooms, shops, control rooms, and other "clean" areas in coal conversion facilities, and to monitor skin contamination of coal plant workers. The currently used method of detecting contamination is to turn off ambient lighting and scan the suspected area with a black light. In contrast, the newly developed spotter (a) can be operated outdoors in direct sunlight or indoors in the presence of strong background illumination; (b) provides

a quantitative measure of the amount of fluorescent material; (c) will discriminate between the fluorescence of organic materials and some inorganic compounds based on their fluorescence lifetimes; and (d) does not present a vision hazard to personnel.

II. Experimental

The spotter induces and detects the fluorescence of PNAs that characteristically absorb light in the 350-to 440-nm region of the spectrum and fluoresce with high efficiency in the blue-green region of the spectrum. Multiring heteroatom aromatic compounds, including acridines, are also detected, although they generally absorb light and fluoresce at longer wavelengths than do their pure hydrocarbon counterparts.

The optics unit, shown schematically in Figure 2 serves two functions. It is: (a) an illuminator, which produces a beam of amplitude-modulated fluorescence exciting light; and (b) a fluorescence detector, which responds to filter selected wavelengths bands in the 380- to 600-nm range. The fluorescence exciting light is one of the emission bands produced by a high pressure mercury arc lamp, typically the 365-nm band for PNAs. The lamp output is focussed onto vanes of a fixed frequency electromagnetic chopper, and subsequently collimated and filtered. This beam reflects off a 96% reflector and is then focused onto a dichromatic beam splitter appropriate to the selected excitation and emission wavelength bands. The reflected excitation beam is output via a telephoto objective lens which can be adjusted to give the desired excitation beam divergence. When the telephoto lens is adjusted to produce a collimated excitation beam, the beam diameter is approximately 1.55 cm. The 96% reflector passes a small percentage of the excitation beam which is measured by an integrated photodiode/op-amp. This signal is used to offset the photomultiplier

signal component due to beam splitter and telephoto fluorescence, and to normalize the resultant fluorescence signal by the excitation beam intensity. Sample fluorescence is collected by the telephoto objective, transmitted through the dichromatic splitter, filtered, and subsequently transmitted to the photomultiplier tube, which converts the fluorescence emission into a photocurrent.

The operation of the spotter is depicted in Figure 3, as are the signal traces corresponding to the radiated uv intensity (trace A) and to the fluorescence (trace B) that is produced when a spill has been "sighted." The radiated uv beam is amplitude-modulated at 1 kHz by the electromagnetic chopper; thus the induced fluorescence is also modulated at 1 kHz. This 1-kHz fluorescence signal is superimposed on a much stronger signal from reflected background illumination of the viewed surface. The electronic frequency spectrum of ac-powered fluorescent or incandescent room lighting consists of a 120-Hz frequency component and its harmonics superimposed on white noise (dc-powered lamps and sunlight produce only white-noise backgound); hence, it is possible to separate the fluorescence signal from the background signal by electronic filtering (trace C). Demodulating and low-pass filtering of this signal (trace D) effectively averages each 1/2-msec pulse and allows detection of fluorescence only 3% as intense as the background illumination in the optical wavelength band of interest.

The signal processing circuitry is schematized in Figure 4. The photocurrents of both photodetectors are converted to voltages by current preamplifiers, and the two signals subsequently fed to a differential amplifier. During spotter operation the null potentiometer is adjusted to produce the minimum LCD meter output with the spotter head pointed

at an infinitely distance surface. This difference signal is fed to a phase sensitive demodulator which is gated by a reference signal from the beam chopper oscillator. The output voltages from the demodulator card, which are the sine and cosine phase components of the difference singal are either routed directly to a 3-position output selector switch or, are processed by analog circuitry which computes the difference signal amplitude as the square root of the sum of the squares of the two phase components. The selected output is then inverted and fed into the numerator input of an analog divider. The dc voltage output of peak detector circuit, which measures the height of the excitation intensity pulses, feeds the denominator input of the divider, whose output is now independent of the mercury lamp output power. This voltage, which has now been compensated for background fluorescence and excitation intensity variation, is read out via a voltage-to-frequency converter coupled to a small speaker and a digital voltmeter. In actual operation, the user scans the suspect surface with the optics head, and upon locating an area which produces a significant increase in the frequency or the audio output tone, reads the voltage level on the meter. Precalibration of the instrument with a known standard enables conversion of the meter voltages to contamination levels in equivalent units of the standard compound.

III. RESULTS AND DISCUSSION

The spotter has been laboratory tested with pure compounds and with several coal and oil shale products and wastes. When operated in a laboratory area illuminated by fluorescent lighting, the spotter can typically detect 0.1 μg of perylene (as a dilute solution in cyclohexane) located 50 cm distant. Considering that 10 μg doses of several PNAs will induce

changes in the metabolism of cultured mammalian cells (3,4), it is evident that the high sensitivity of the spotter is appropriate to its intended task. In this regard the spotter might prove to be particularly useful in quantitatively measuring PNA skin contamination caused by contact with coal derived liquids, thus providing accurate data for correlation with the incidence of skin lesions. The currently used technique in at least one coal liquefaction facility is to periodically scan workers with a short or long wave black light in a darkened room, and to visually estimate the extent of contamination (7). Possible co-carcinogenic effects due to exposing contaminated skin to the spotter's uv beam should be negligable, due to the limited exposure of the person to the beam, whose intensity is only .93 mW/cm^2, 3-6X less than the uv intensity of sunlight in the 350-400 nm wavelength band (8). Accurate measurements of skin contamination will enable evaluation of the effectiveness of various coal plant health protection practices such as the types of protective clothing used, the use of barrier creams, and the usefulness of different methods of cleaning contaminated skin.

The dynamic range of the spotter's response is 0.1 μg perylene to greater than 10 μg perylene (at 50 cm distance) as can be ascertained from the data shown in Figure 5. The distance dependance of the signal from a 10 μg sample is shown in Figure 6 for the condition where the telephoto output lens is adjusted so as to produce a collimated uv beam. The signal decrease below the $(distance)^{-2}$ power law at distances beyond 60 cm is due to some residual divergence of the uv beam caused by the finite size of the beam focus on the dichromatic splitter.

Tables I and II list the spotter-measured specific fluorescence of several synthetic fuel products and wastes. The oil samples were prepared

by placing 1- to 10-mg droplets of each oil onto microscope slides and covering each with a cover slip. This technique yielded 1- to 20-μm thick films of known area and thickness whose optical absorbance at 365 nm, the principal excitation wavelength, was less than 0.3-o.d. units. The undiluted waste samples were placed into 3.6-cc vials for measurement, with the exception of the surge-tank sludge which was diluted 400:1 in cyclohexane. The variation in the specific fluorescence of the SRC-I recycle solvent, wash solvent, and light oil (Table I) parallels preliminary determination of their 1,2-benzpyrene (BP) content (5). This is noteworthy because consideration is being given to the use of BP as the proxy compound for PNA determination in coal and oil-shale derived liquids (6).

Milligram-level films of Oak Ridge National Laboratory (ORNL) hydrocarbonization oil and COED syncrude on both floor tile and metallic surfaces have also been examined in a less quantitative fashion. The film fluorescence was at least ten times stronger than the substrate fluorescence, which made the "spots" readily distinguishable. Preliminary field testing work with the spotter, carried out in the ORNL hydrocarbonization facility, detected milligram-level coal tar contamination on the plumbing and floor.

Coal liquefaction products may contain certain organic compounds, heavy-metal inorganic materials, and particulate matter, all of which quench the fluorescence of PNAs and thus interfere with fluorometric monitoring techniques. Two such classes of aromatic compounds abundant in coal conversion products are simple phenols and acridines. We have tested for phenolic intereference by adding large excesses of phenol to solutions containing perylene. Phenol did not interfere with our fluorometric PNA determination. However, heteroatom aromatic compounds such as

acridines, which are abundant in oils having a high asphaltene content and whose absorption maxima overlap the emission maxima for PNAs, may partially quench PNA fluorescence. This quenching may partially explain the decreased sensitivity of the spotter to ORNL hydrocarbonization oil and to SRC-I light organic liquid (Table 1). Both materials undergo a large increase in specific fluorescence when dissolved in cyclohexane.

The spotter is capable of discriminating between classes of organic contaminants, such as PNAs and acridine dyes, by selecting optimal excitation and emission wavelengths with optical filters. The spotter can also discriminate the fluorescence of inorganic materials such as uranyl nitrate from the fluorescence of organic compounds, although both materials have similar optical properties, due to the long luminescence lifetime of uranyl nitrate. The delayed fluorescence of uranyl nitrate results in a phase shift in its fluorescence signal relative to the fluorescence signal from organic compounds. Thus the relative amplitudes of the two phase component output voltages from the phase sensitive demodulator will be different for the two types of fluorescent material. The spotter is sensitive to 1-mg quantities of uranyl nitrate and could conceivably be used to locate spills or leakage in nuclear-fuel and waste-handling facilities. This phase-shift measurement capability of the spotter may also be useful for discriminating PNA fluorescence from background luminescence from inorganic pigments commonly used in paints.

V. Future Developments

An extensive field testing program for the fluorescence spotter will begin during FY 1980, in order to assess the usefulness of the spotter to fossil energy conversion plant health protection programs. Two advanced version spotters which can operate either from ac power or from batteries are currently being

fabricated at ORNL. Planning for on-site testing at the PAMCO SRC pilot plant at Ft. Lewis, Washington, the Pittsburgh and Morgantown Energy Technology Centers, and the Hygas Coal Gasification Pilot Plant in Chicago is underway. Field testing program activities will include monitoring PNA contamination on surfaces in various plant facilities and monitoring plant personnel for skin contamination. The data gathered in this program should be useful for correlation with in-plant air monitoring PNA measurements, for correlation with the incidence of skin or respiratory health problems, and in the establishment of good housekeeping and health protection practices in such facilities.

Acknowledgements

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Fig. 1. Portable fluorescence spotter.

Fig. 2. Spotter optics unit.

Fig. 3. Principle of operation of spotter.

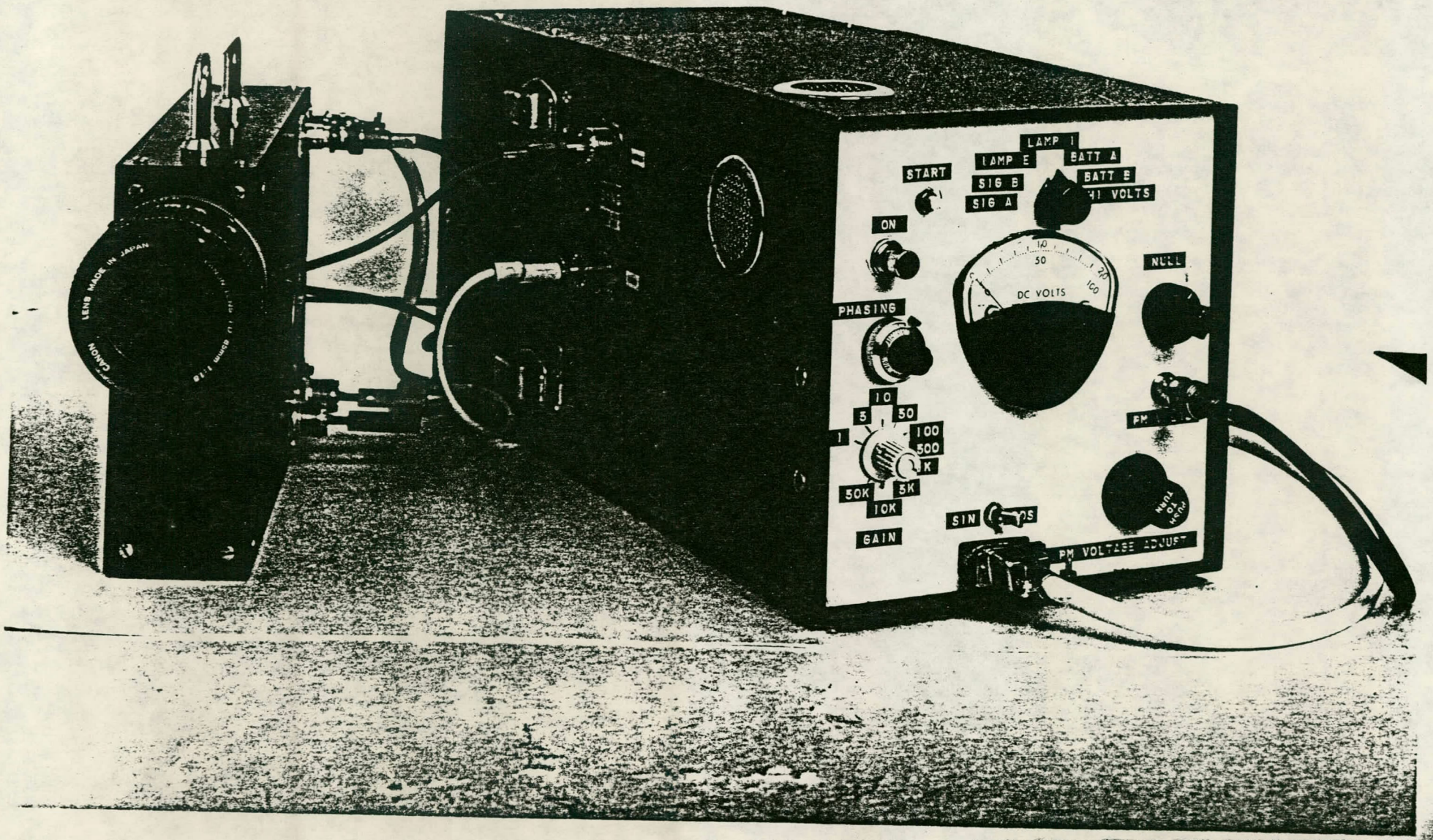
Fig. 4. Spotter signal processing circuitry.

Fig. 5. Spotter response vs sample PNA content. The samples were 0.064-6.4 ppm solutions of perylene in cyclohexane.

Fig. 6. Distance dependence of spotter response.

Table I. Specific fluorescence of various fossil fuel oils and process solvents.

Table II. Specific fluorescence of coal liquefaction wastes.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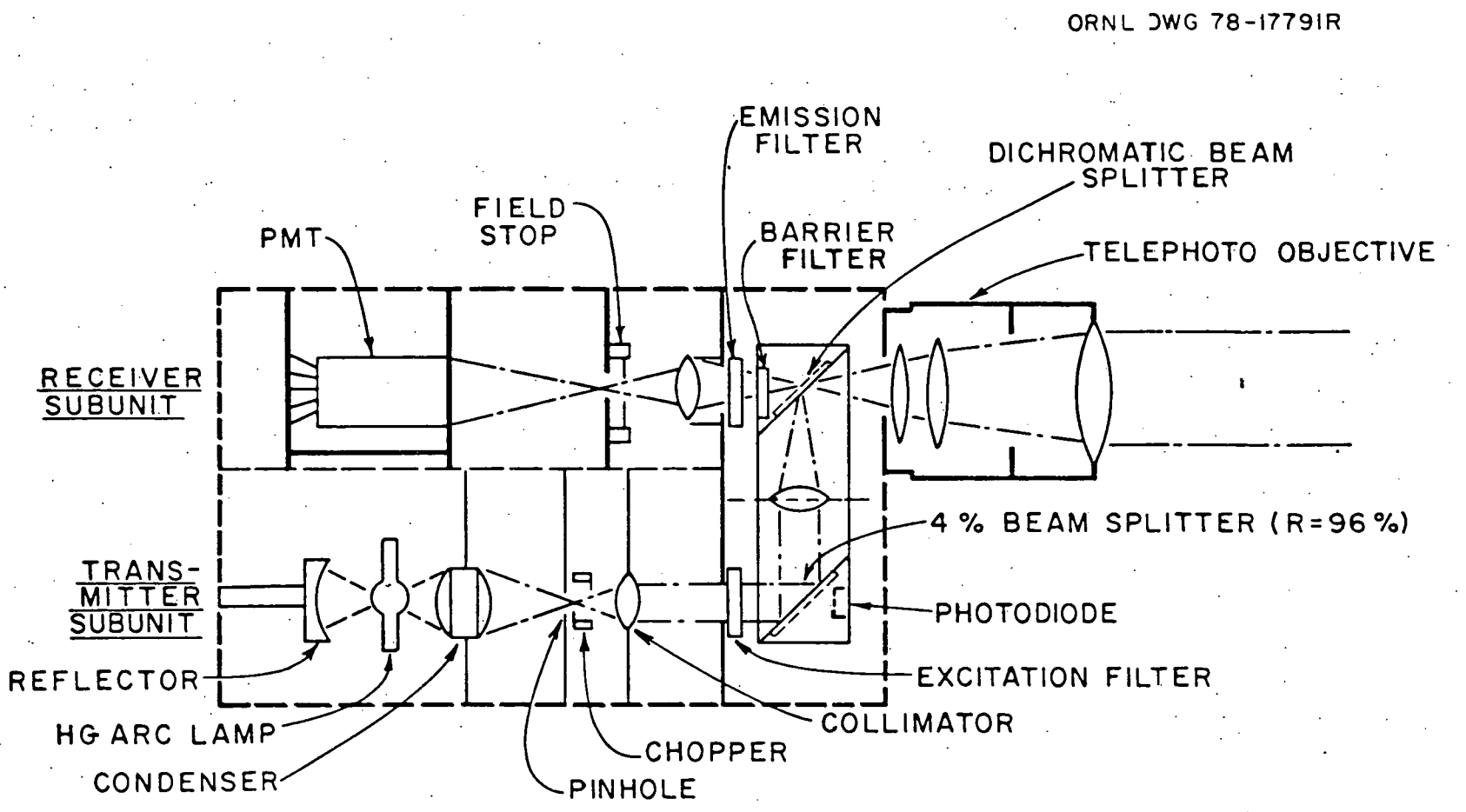
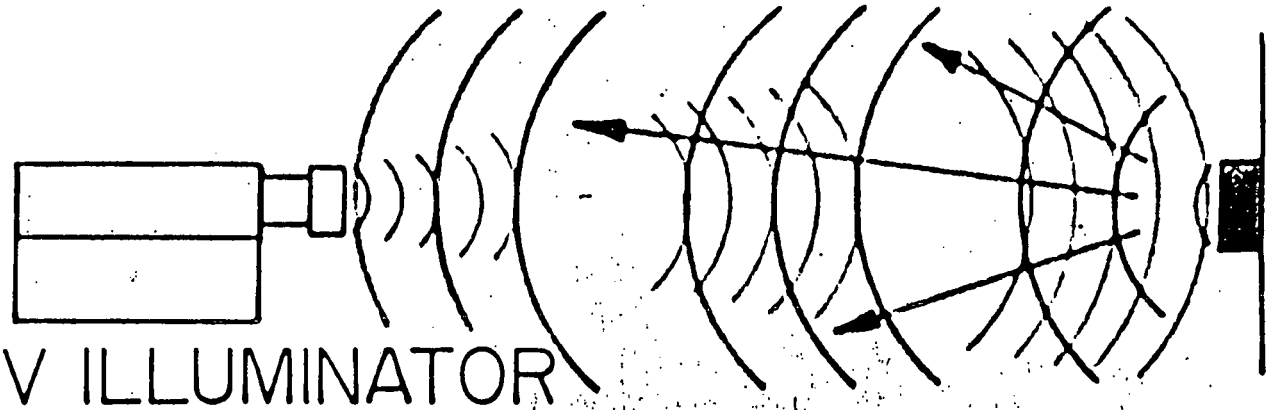

ORNL DWG 78-17791R
EMISSION FILTER
DICHROMATIC BEAM SPLITTER
FIELD STOP
PMT
BARRIER FILTER
TELEPHOTO OBJECTIVE
RECEIVER SUBUNIT
4 % BEAM SPLITTER (R=96 %)
TRANS-MITTER SUBUNIT
PHOTODIODE
REFLECTOR
EXCITATION FILTER
HG ARC LAMP
COLLIMATOR
CONDENSER
CHOPPER
PINHOLE

FLUORESCENCE
RECEIVER



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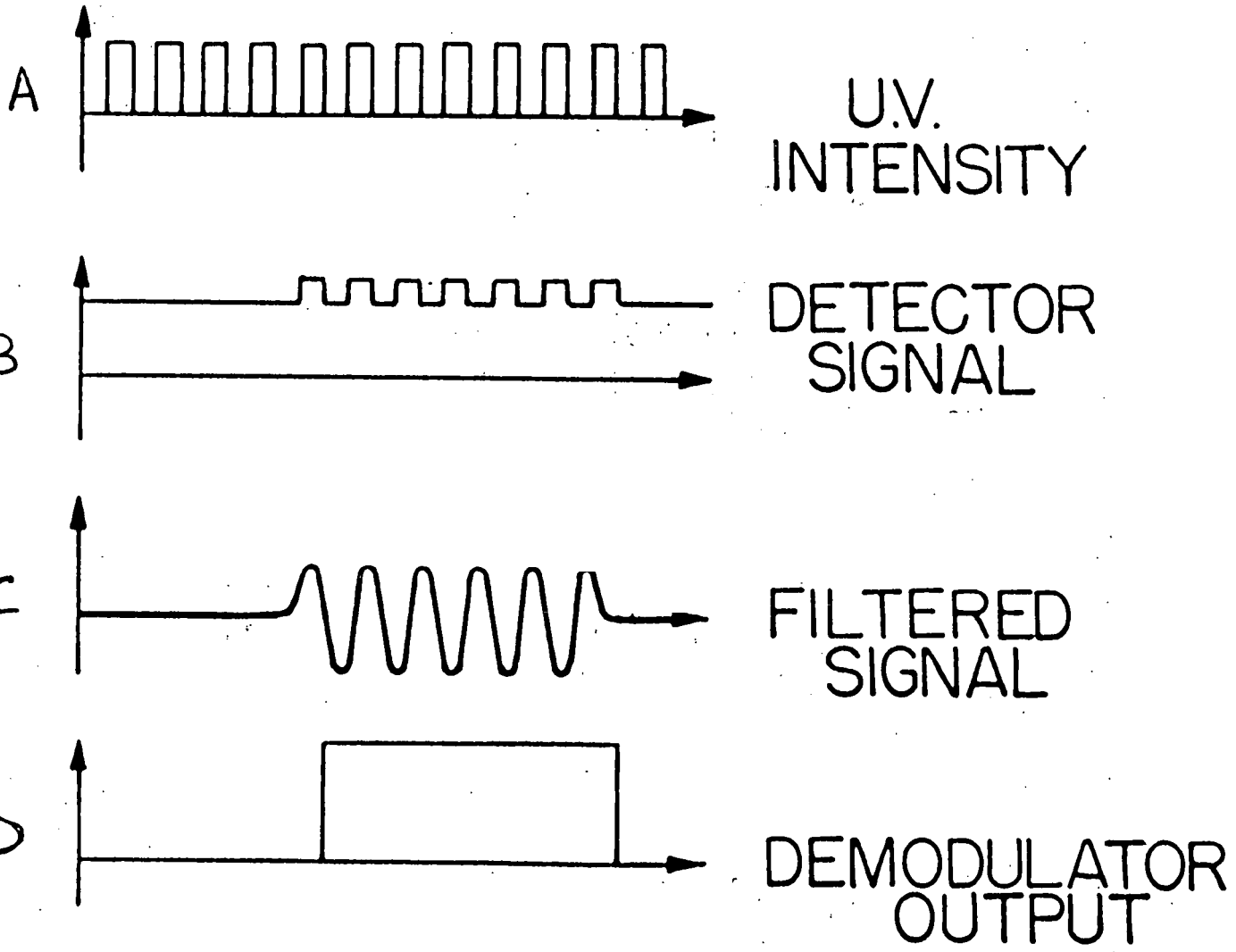

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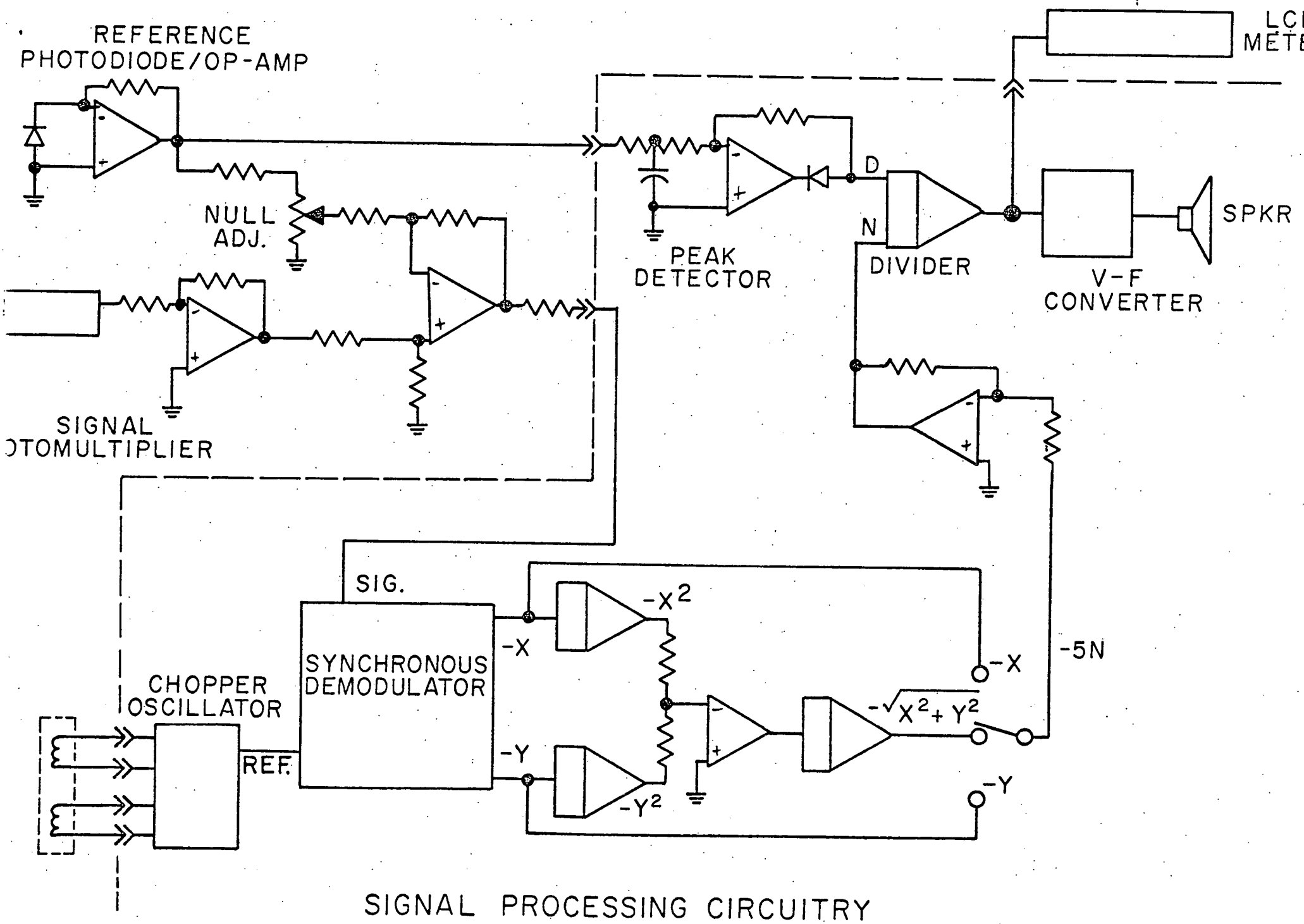
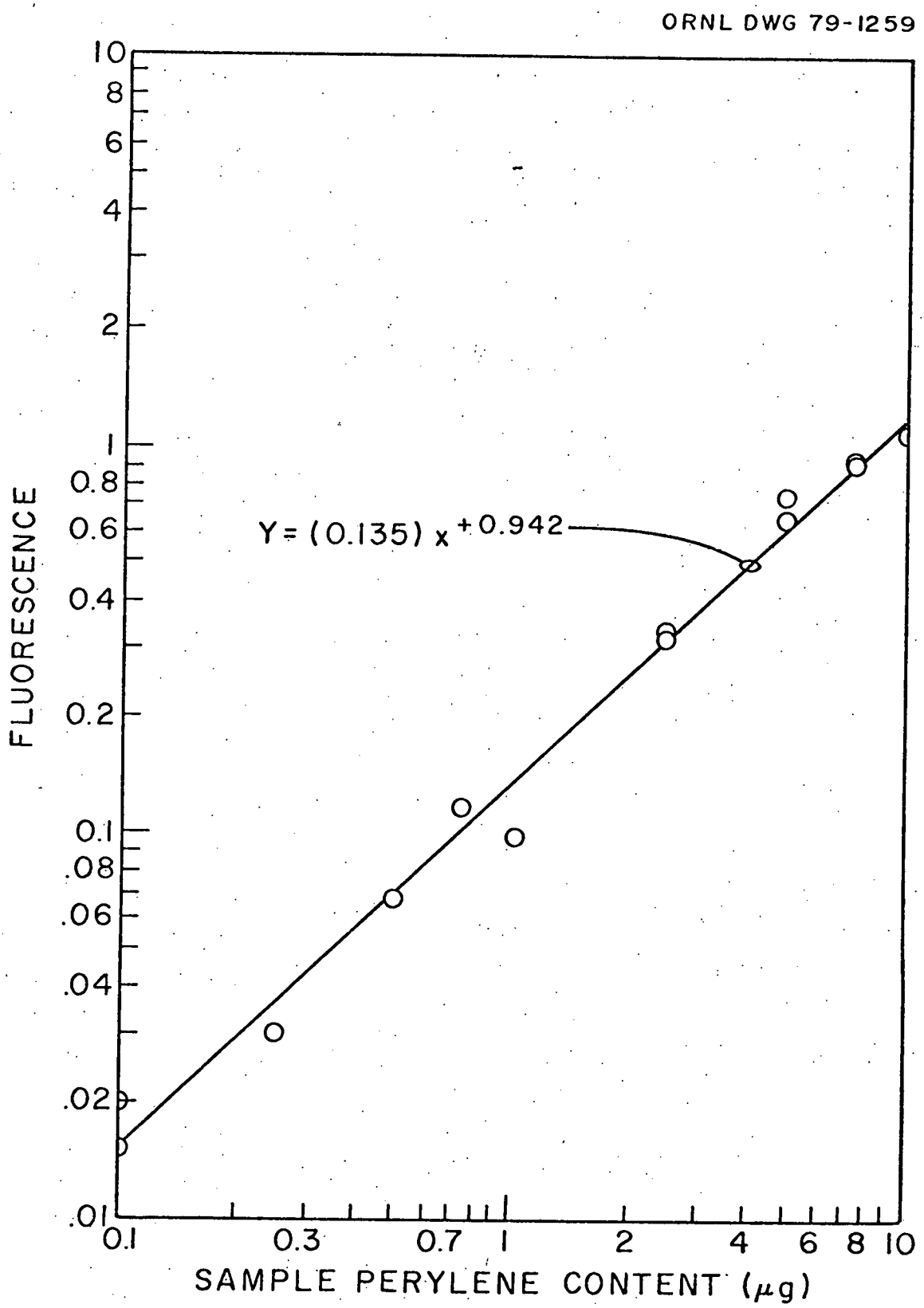


SIGNAL PROCESSING CIRCUITRY


ORNL DWG 79-1259
FLUORESCENCE
SAMPLE PERYLENE CONTENT (μg)
Y = (0.135) x + 0.942
10
8
6
4
2
1
0.8
0.6
0.4
0.2
0.1
.08
.06
.04
.02
.01
0.1
0.3
0.7
1
2
4
6
8
10

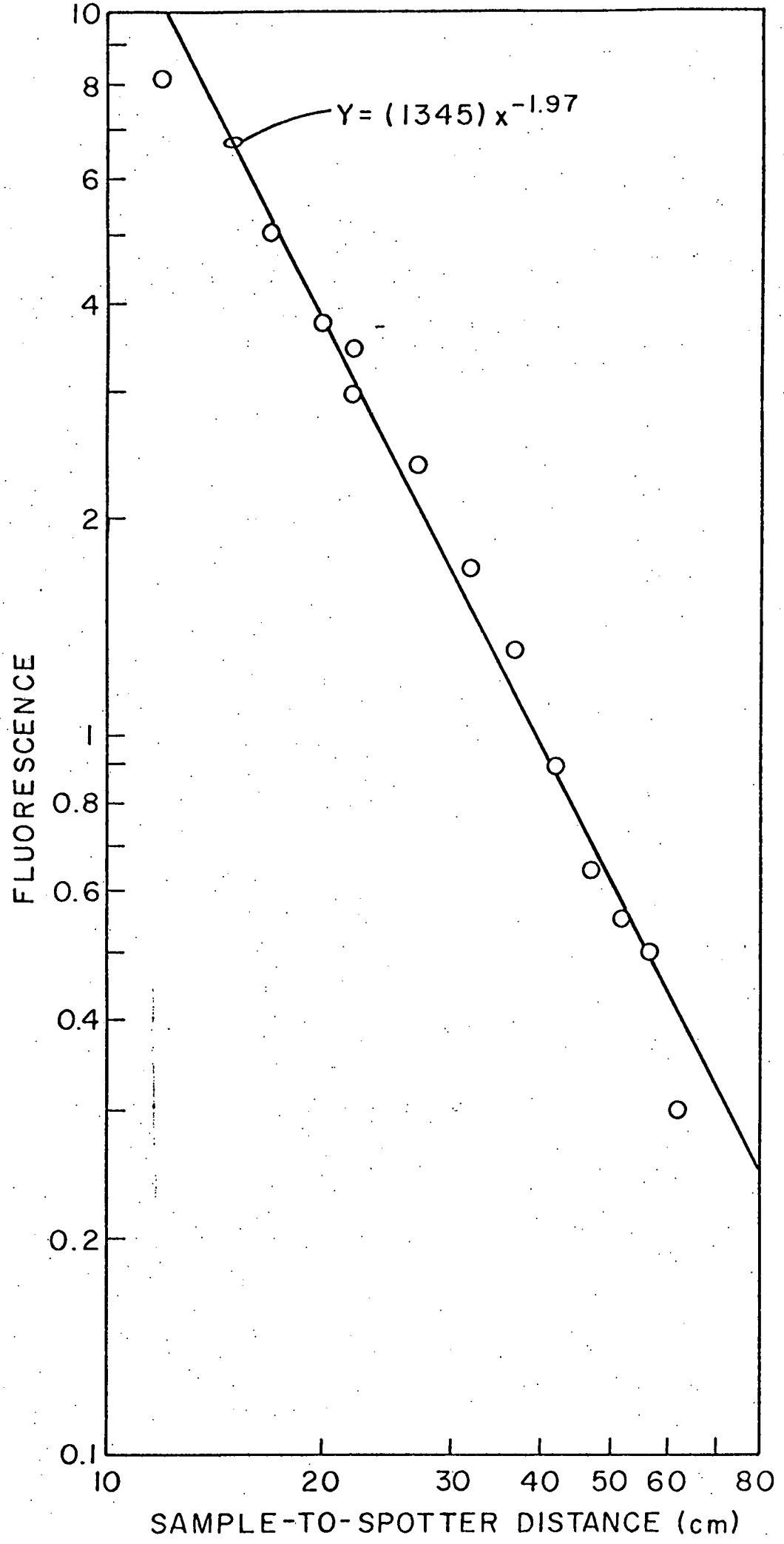

Y = (1345) x^-1.97
FLUORESCENCE
10
8
6
4
2
1
0.8
0.6
0.4
0.2
0.1
10
20
30
40
50
60
80
SAMPLE-TO-SPOTTER DISTANCE (cm)

Table I. Specific Fluorescence of Coal Liquefaction and Oil Shale Products

sample	specific fluorescence,[a] units/mg
COED syncrude	6.3
hydrotreated coal distillate	3.4
product distillate	11.3
centrifuged shale oil	4.8
ORNL hydrocarbonization oil (HC-12)	0.2
SRC-II fuel oil blend	7.7
SRC-I recycle solvent (raw)	4.6
SRC-I wash solvent	0.9
SRC-I light organic liquid (raw)	0.1
SRC-I process solvent	3.7
SRC-I light oil	b

[a]One unit of fluorescence is defined as the equivalent fluorescence of 1 µg of perylene in dilute solution in cyclohexane.

[b]Not detectable.

Table II. Specific Fluorescence of Coal Liquefaction Wastes

sample	specific fluorescence,[a] units/mg
SRC-I bio-unit feed	0.7×10^{-3}
SRC-I bio-unit effluent	0.4×10^{-3}
SRC-I bio-unit sludge	1.9×10^{-3}
SRC-I plant effluent	b
SRC-I surge tank sludge (diluted 400:1 in cyclohexane)	12.9×10^{-3}
SRC-I surge reservoir water	0.7×10^{-3}
SRC-I graver effluent	0.6×10^{-3}

[a]One unit of fluorescence is defined as the equivalent fluorescence of 1 µg of perylene in dilute solution in cyclohexane.

[b]Not detectable.