RESEARCH Report for SBIR Grant Phase I

A simple device for measuring personal exposures to UV

Stanley D. Echols, Riverbend Instruments Inc.
Ronald Rahn, Dept of Environmental Health, Univ. AL at Bhm.

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Abstract

The research carried out here was in response to the request by NIOSH to develop easy-to-use, direct-reading instruments and test kits for measuring exposures rapidly and inexpensively in a variety of workplaces for routine monitoring. This directive, in part, follows from the workshop hazards conference in Chicago in March 1998 sponsored by NIOSH in which non-ionizing radiation was identified as one the 6 priority areas for further study and research. Development of methodology to aid in the exposure assessment of ultraviolet radiation in the workplace is the goal of the work carried out in this phase I SBIR proposal.

UV exposure or dose can be measured with either an electronic metering device such as a radiometer, or by means of chemical actinometry in which an aqueous solution upon irradiation undergoes a measurable change detected by absorbance or fluorescence. Rahn (see references) has described the use of chemical actinometers which utilize the formation of triiodide as an endpoint which is easily measured by absorption spectroscopy. Triiodide is formed when either iodouracil (IU) is irradiated in the presence of iodide (I-) or when iodide is irradiated in the presence of an electron scavenger such as iodate. Triiodide can be measured using its absorbance maximum at 352 nm. From this measurement, carried out using 1-cm path quartz optical cells for both irradiation and absorbance measurements, the UV fluence can be determined.

In order to develop an inexpensive and portable light-detection device, we have decided to use as the light source a light emitting diode (LED). Because LEDs are not available at 352 nm where triiodide absorbs, thyodene, a starch derivative, was used to react with triiodide to form the starch iodine complex, which absorbs strongly at 470 nm, a wavelength at which an LED is commercially available.

The research carried out here demonstrates that chemical actinometry using 3 mm ID quartz tubes along with a photometer constructed from a light emitting diode and a light sensitive diode, constitutes an inexpensive, accurate system capable of determining the exposure of workers to ultraviolet hazards. The prototype photometer developed here utilizes recently available light emitting diodes and a light sensitive chip to measure the UV-induced formation of

the starch-iodine complex. Individuals in the workplace where UV radiation is present may wear quartz tubes, used to hold the actinometric solutions. The change in the absorbance of the solution due to the formation of triiodide and its reaction with starch can then be monitored using the photometer developed here.

The following objectives were accomplished:

(1) A photometer was constructed with inexpensive components for use with chemical actinometers to permit quantitation of accumulated dose of UV-B and/or UV-C.

(2) The photometer design was optimized for reproducibility and its dynamic range and linear response characteristics determined. Also, the effect of ambient temperature on the instrument response was measured.

(3) The feasibility of using small quartz tubes for long-term storage, radiation exposure and photometric measurements of the actinometric solutions was demonstrated.

(4) Tubes filled with the actinometric solution containing thyodene were irradiated and the absorbance measured in the prototype photometer as a function of the fluence determined using a radiometer. The results were compared with the same solution irradiated in 1-cm quartz cuvettes and measured in a commercial spectrophotometer. The results demonstrate an equivalency between the two methods of measurement. Hence, the prototype system proposed here can be used to determine accurately UV fluence using chemical actinometry.

(5) The effect of temperature on the long-term stability of the actinometric solutions was determined by holding samples of either iodide/iodate or iodouracil/iodide at either 8 C or room temperature for up to 7 weeks. Only the iodide/iodate solution showed appreciable formation of triiodide upon storage. The rate of this spontaneous thermal oxidation process was reduced 2-fold at 8 C. The slope of the dose response curves showed at most a small effect of storage provided background corrections were made.

Significant Findings

Fluence measurement of UV-B and UV-C are feasible by means of the following method: actinometric solutions in inexpensive quartz tubes of 3 mm inside diameter are exposed to UV and absorbances are measured in an inexpensive photometer. The observed absorbance change is proportional to fluence. Our prototype photometer uses a common LED with a 470nm wavelength and a light-intensity-to-frequency chip.

Temperature stability of the prototype photometer was good, and the dynamic range when used to read absorbance of the starch-iodine complex, the species produced by both of the actinometric solutions studied, was more than adequate for personal dosimetry.

Measurements of UV-C fluence performed by irradiating actinometric solutions in small quartz tubes yielded values very close to those obtained with a radiometer. Spinning the tubes during photometry increased the precision of the measurements. If account of light path length is taken, absorbance measured by our system is very close to that measured in a cuvette in a standard spectrophotometer.

We found that, to behave linearly, the actinometric solutions needed a higher thyodene concentration than the 16 mg/ml that we originally used.

As noted previously, the absorbance of the iodine/iodate actinometric solutions, which have been exposed to UV-C, varies appreciably with temperature. The dissociation of the starch-iodine complex appears to account for this effect.

The iodouracil system that responds to UV-B is stable for at least seven weeks when stored in quartz tubes at room temperature. The iodine/iodate system undergoes spontaneous darkening while stored in quartz tubes: three weeks of storage at room temperature is roughly equivalent to 30 seconds of exposure to a 15-wztt germicidal lamp at a one foot distance. Storage at 8 C. approximately halved the rate of spontaneous darkening. Darkened tubes still yield correct dose measurements if absorbance before irradiation is taken into account.

Usefulness of Findings

The results obtained suggest that this system can be used to monitor worker exposure to

UV-C. Because of the linear response of the system to UV-fluence, these tubes can be worn and the exposure to UV integrated over time. Measurements with the photometer at the beginning and end of the day can then be used to obtain a measure of UV exposure over an 8-hour period. The sensitivity of the system is such that current NIOSH exposure limits (~ 8 - 9 millijoules/cm^2) are easily measured. It is expected that materials and devices can be supplied allowing workers to prepare solutions, fill tubes, and carry out exposure measurements.

Although the majority of the work carried out here involved UV-C as measured using the iodide/iodate system, UV-B measurements can also be done using the iodouracil/iodide system. The end result in both cases is the same, namely the starch-iodine complex formed by triiodide in the presence of thyodene.

Scientific Report

Aim 1: To construct a photometer with inexpensive components for use with chemical actinometers to permit quantitation of accumulated dose of UV-B and UV-C.

A schematic design for the prototype photometer is given in Figure 1. It consists of two units, the optical unit and the electronic unit made up of the controller and the counter/readout. The optical portion is designed to use small quartz tubes to hold the aqueous actinometric solution. The light source, slits, holder for quartz tubes, and photodetector, form a separate unit. The output wavelengths available from inexpensive light emitting diodes (LEDs) of high brightness are limited. Of the emission wavelengths available, the optimum for measuring the starch-iodine complex is centered around 470 nm with a bandwidth of approximately 20 nm. While light of this wavelength is not strongly absorbed by triiodide itself, it is ideal for measuring the starch-iodine complex, which absorbs strongly in this wavelength region.

The rest of the system consisting of the controller and the counter/readout or display are housed in a separate box connected with ribbon cable. It is anticipated that the production model would be a single, compact unit. The light intensity readout is in units of frequency, which corresponds to the number of pulses per second. Although a one-shot chip to time the counting interval was originally proposed, it was felt that the counting interval would vary too much with temperature. Hence, a crystal oscillator, which is far more temperature stable, and a divider was used to generate the counting interval.

Aim 2: To optimize the photometer design, determine its dynamic range and linear response characteristics, and measure the effects of ambient temperature on the instrument response.

A. Design optimization

To improve reproducibility, it was necessary to develop a method that would hold each sample tube firmly and in a reproducible position. For this purpose a piece of brass angle stock,

as shown in Fig 2, was used as a guide to hold the quartz tube in place. A flat spring holds the tube against the corner of the angle stock into which a slit 1.5-mm in width and 4 mm in height is cut. This second slit is opposite the slit in the brass tube containing the LED.

B. Determination of dynamic range and linearity of response.

Having optimized the design of the photometer, it was of interest to determine the dynamic range and linearity of response. Hence, varying concentrations of the starch-iodine complex were prepared and the absorbance of these samples was measured at 470 nm in a conventional spectrophotometer using either 1 cm or 1 mm path quartz cells. The results are presented in Table 1. The samples were then placed into quartz tubes (4 mm OD and 3 mm ID) and the absorbance measured in the same spectrophotometer using a special holder for the sample tubes. These results are also shown in Table 1. The ratio of the absorbance as measured in the tubes relative to that in the cell was on average, as indicated in the Table 0.302.

Absorbance measurements were then carried out on the same samples contained in the tubes using the prototype photometer. The results are presented in Table 2. The absorbance A is obtained as follows: the transmission of light through the sample tube is proportional to the output of the light to frequency chip. Frequency varies directly with light intensity. A quartz tube filled with water was taken as the 100% transmission value. Its frequency was on the order of 70,000 Hz. For zero transmission (i.e. the dark current) we used a quartz tube filled with India ink which gave a frequency of 32 Hz. This same frequency was obtained upon dilution of the sample several-fold. Hence, 32 Hz represents 0 % transmission. The dynamic range is therefore approximately 2000-fold (70,000/32). This result implies that very little stray light reaches the photodetector even though no attempts were made to shield the instrument from room light.

To convert light transmission data to absorbances, the following expression is used

$$\text{Absorbance} = \log 1/T$$

where $T = f/f'$, f is the frequency of the unknown sample and f' is the frequency of the blank or water solution, both of which are corrected for a dark current or background contribution of 32 Hz. In this way the frequency values shown in Table 2 were converted into absorbance values. Also shown in Table 2 are the absorbance measurements made in the spectrophotometer using conventional flat cells and normalized to a 1-cm path. The ratio of the photometer values to these

spectrophotometer values is given in the Table and as indicated the average value for this ratio is 0.300, same as found in Table 1. Hence, the photometer and spectrophotometer measurements are in good agreement, and are in agreement with the pathlength in the tubes being 3 mm.

The absorbance values obtained with tubes are plotted in Fig. 5 as a function of the absorbance at 470 nm in a 1 cm cell in order to compare once again spectrophotometer measurements at 470 nm with photometer measurements using the 470 nm LED. As expected, based on the above analysis, curves a and b lie virtually on top of each other suggesting that the photometer data are quite comparable to those obtained with a conventional spectrophotometer. In fact, it appears that linearity holds over a greater range for the photometer than the spectrophotometer, although this may be a result of the optics of the photometer being designed to measure the transmission of small tubes whereas the spectrophotometer is designed to measure the absorbance of conventional rectangular cells.

Effect of ambient temperature on instrument response.

Two unrelated substances were used to distinguish thermal effects on the instrument from those on the samples. Solutions of cobalt chloride and of Quink brand ink were adjusted so that about 50% of incident light was transmitted as measured in the photometer. It is assumed for both of these solutions that the absorbance is temperature independent. These samples were then read with the prototype photometer at room temperature (23 C.), and then at either 37 C or 7 C after a 20-minute equilibration. It was felt that the components in the electronic portion of the photometer should be temperature independent. In the optical unit, the light intensity to frequency chip has excellent temperature stability. However, the effect of temperature on the light output of the LED needed to be examined. Hence, the optical part of the photometer was held at these different temperatures to test this out. The data as shown in Table 3 indicate that the response of the photometer is temperature independent. However, the same is not true of the actinometeric solutions themselves as we point out later.

At this point, the components and design features of the photometer are reasonably well set and it is of interest to assess the costs of such a device. The optical components are very inexpensive: the component cost of the entire optical part is less than twenty dollars, and no very precise manufacturing methods should be necessary. As mentioned in our proposal, we expect a

production model to employ a microprocessor rather than the logic and counter/readout chips of the present prototype. The microprocessor component would probably be somewhat more expensive than the optical part, but the parts and manufacturing costs of a complete production model seem likely to be on the order of $100 or less.

Aim 3 To determine, for commercial purposes, the feasibility of using small quartz tubes for long-term storage, radiation exposure and photometric measurement of the actinometric solutions.

Tube Preparation

Sample tubes were made by cutting 3 mm I.D. quartz tubing into about 5 cm. lengths. One end was sealed in an oxyacetylene flame. Because of the nonuniformity of the ID of the quartz tubing, it was important to investigate the influence of size on the response. Tubes were sorted using drill bit sizes #30-36. The tubes were filled with a solution of the starch-iodine complex and the absorbance measured in the photometer. The results are given in Figure 6. As observed there is a linear increase in the absorbance consistent with the increase in the diameter of the tube. Hence, tubes need to be selected on the basis of their diameter. To obtain a set of tubes of the same diameter, selection is done using a #32 drill bit (2.95 mm) but not a # 31 drill bit (3.04 mm) to match the ID. This selection process limits tubes to a range of 2.95 – 3.04 ID. Tubing in 48-inch lengths can be obtained from National Scientific Quartz with 4 mm OD and 3 mm ID. The variation in ID within a given lot of tubing is such that half the tubing fits a # 32 drill but not a # 31 drill. Tubes were sealed at one end using a oxy-acetylene torch. After filling the tubes with the actinometric solution, they were sealed with parafilm.

Long-term storage

The use of tubes as vessels for long-term storage will be addressed in Aim 5

Radiation Exposure

Iodouracil/iodide actinometers in tubes were held in a wire frame 3 inches from the surface of a Westinghouse FS 20 sunlamp. Absorbance data were generated before irradiation and after each of four consecutive irradiation periods of 15-minute duration. The experimental design for the iodine/iodate actinometers was similar except that the actinometers were supported 12 inches from a

GE G25T8 15 W low-pressure mercury lamp with a predominant output at 254 nm. Absorbance data were generated before irradiation, and after each of 4 consecutive irradiations of 30-second duration.

Photometric measurement.

It was felt that spinning the tubes about their axis during measurement lessened the scatter of data from the prototype photometer. This has the effect of averaging the characteristics of the light path over all angles of the tubes, thus lessening the effect of optical irregularities. In the data presented previously, all tubes were spun by hand during measurement in the photometer. Here, we wish to establish in a more systematic manner the effect of spinning the tubes during measurement.

A set of 9 tubes containing the iodide/iodate actinometeric solution was exposed to various levels of radiation so as to obtain a set of samples of varying absorbance. The raw data from the photometer varied from about 66,000 Hz for the unexposed actinometer down to about 24,000 for the highest level of irradiation. Then each tube was placed in the prototype photometer, four measurements made at a fixed position, four single measurements made at four different angles, and four measurements made while spinning the tube. Spinning consisted of twirling the tube by hand during the 1-second measurement interval. Approximately 2-3 complete rotations occurred during this time interval.

The measurements are presented in Table 4 and standard error estimates were calculated with the technique of analysis of variance. The standard deviation for tubes left in the same orientation for all four measurements gave an estimate of the intrinsic noise of the system. This orientation-independent value corresponds to a standard deviation of 47 Hz, which is roughly one thousandth of the mean, indicating very low system noise. The standard deviation estimates from spun tubes was 127 Hz, or roughly one eighth the value from tubes inserted at arbitrary angles: 998 Hz.

To relate these standard deviation of frequencies to corresponding absorbances involves a nonlinear function (i.e. A~log 1/frequency), so the results depend on the magnitude of the absorbance. It is concluded that for transmission of half of the incident light in our tubes, which is in the range we expect to employ, a difference of 100 Hz in our system translates to an absorbance

difference of about 0.002, which is quite small. Hence, spinning does reduced the variance and should provide a more precise as well as accurate measurement of the absorbance of the solution.

Aim 4: To compare the photometric response of the exposed actinometers with the radiation dose as determined with a radiometer.

The purpose of this aim is to examine the UV response of the actinonometric solution when irradiated in quartz tubes and the absorbance measured using the prototype photometer described here. The question to be addressed is whether this system can be used to obtain an accurate value for the UV fluence.

It has been well established that the iodide/iodate actinometric solution can be used to measure the fluence of a low-pressure mercury lamp. These measurements have done in the absence of thyodene by measuring the absorbance increase at 352 nm. The use of thyodene to form a complex with triiodide only shifts the absorbance maximum to longer wavelengths and requires the use of a different extinction coefficient. The actual absorbance spectrum of the iodide/iodate actinometric solution irradiated in the presence and absence of thyodene, is shown in Figure 7. From these data one calculates the molar absorptivity coefficient for the triiodide-starch complex as 29,900 $M^{-1}cm^{-1}$ as compared with that of 27,300 for triiodide as measured at 352 nm.

The dose response as a function of the UV fluence for a solution of iodide/iodate plus thyodene (15 mg/ml) is shown in Fig. 8. This data was obtained using a 1-cm cell for both irradiating the sample at 254 nm as well as for measuring the absorbance at 470 nm using a conventional spectrophotometer. As indicated the slope is linear and is proportional to the fluence as measured with a radiometer. The slope of this curve is 0.4.

An analogous experiment was done using quartz tubes to hold the sample during irradiation and also to measure the corresponding increase in absorbance using the photometer. As shown in Fig. 9 the corresponding dose response curve (dotted) is nonlinear. This result suggests that the concentration of thyodene was too low. Addition of more thyodene (100 mg/ml) prior to irradiation gives a linear dose response (solid line). The slope of this line is 0.47

It is of interest to compare the slope of the dose response curves in Figures 8 and 9. In the 3-mm ID quartz tubes the rate of photochemical reaction is 4.2 times greater than in a 1-cm cell. This occurs because the cross sectional area exposed to the radiation is 4.2 times greater in the tube than

in the 1-cm path cell for a given volume. On the other hand, the shorter pathlength in the tube (3mm) results in the absorbance being 0.3 of that obtained with a 1 cm cell for a given concentration. Hence, overall one would expect that in the tube the absorbance for a given dose of radiation would be 4.2 x 0.3 = 1.26 times greater than that obtained with a 1 cm path cell. The slopes in Figures 8 and 9 by comparison, 0.4 and 0.47, respectively, give a ratio of 1.17, or relatively close to the theoretical value.

The optical spectrum of the starch-iodine complex is given in Figure 10 showing changes over the temperature range 25 to 65 C. As the solution is heated the complex falls apart and free triiodide is formed. Cooling reverses this process. Only two species are involved as demonstrated by the isosbestic point at 390 nm. A plot of the absorbance changes from 20 to 50 C is given in Figure 11. Examination of the data between 20 and 30 C shows an absorbance change of approximately 0.01 absorbance units per degree C. It remains to be determined whether it will be necessary to compensate for this degree of temperature dependence.

Aim 5: To determine the effect of temperature on the long-term stability of the actinometric solutions.

Relatively long-term stability of both the iodide/iodate and iodouracil/iodide actinometric systems upon storage at room temperature and 8 C was investigated as follows: tubes selected with a #32 drill bit were filled with the actinometric solutions and stored for up to 7 weeks in the dark at either room temperature or 8 C. Measurements were made of duplicates of the unirradiated samples once a week over a 7-week period and the results are shown in Figures 12 and 13. Spontaneous thermal oxidation takes place in the iodide/iodate actinometer with a rate 2-fold greater at room temperature than at 8 C. Three weeks of storage at room temperature is roughly equivalent to a 30-second exposure to the germicidal lamp. Essentially no change takes place in the IU/I samples over the 7-week period.

Dose response curves were also obtained over this same time period for each of the actinometers, using sunlamp radiation (four 15-minute intervals) for the IU/I actinometer (Figs. 14 and 15) and germicidal radiation (four 30-second intervals) for the iodide/iodate actinometer (Fig 16). At one-week intervals, duplicates of each actinometer type were withdrawn, equilibrated at

room temperature, and dose response curves obtained. Slopes of the dose response curves, background corrected, are similar, showing that storage under these conditions has at most a minor effect upon radiation response of either type of actinometer.

References

1. Rahn, R.O. (1993) KI as a Chemical Actinometer. *Photochem. Photobiol.* **58**:874-880
2. Rahn, R.O. (1997): Potassium Iodide as a chemical actinometer for 254 nm radiation: use of iodate as an electron scavenger. *Photochem. Photobiol.* **66**: 450-455.
3. Rahn, R.O., and M.A. Lee: (1998). Iodouracil as a personal dosimeter for solar UVB, *Photochem. Photobiol.* **68**: 173-178
4. Rahn, R.O., S.L. Miller, and P. Xu (1999): Characterization of Room Air Germicidal Ultraviolet Irradiation: Spherical Actinometry and Radiometry. *Photochem. Photobiol.* **70** 314-318

	Absorbances		
sample#	cuvette	qz tube	ratio
1-blank	0.001	0.000	
2	0.035	0.007	0.200
3	0.156	0.044	0.282
4	0.225	0.065	0.289
5	0.372	0.113	0.304
6	0.539	0.163	0.302
7	0.815	0.256	0.314
8	1.190	0.369	0.310
9	1.602	0.506	0.316
10	2.120	0.681	0.321
11	2.440	0.811	0.332
12	3.020	0.979	0.324
13	4.090	1.281	0.313
14	5.280	1.658	0.314
15	6.570	2.039	0.310
16	10.970	3.224	
17	13.660	3.556	mean
18	15.540	3.556	0.302
19	18.410	3.556	

Table 1. Comparison of absorbance measurements of starch iodine complex in quartz tubes with measurements of the same solutions in 0.1- or 1-cm cuvettes; both measurements made in the spectrophotometer.

	Spectrophotometer	Prototype photometer		
sample#	absorbance cuvette	freq.	absorbance	absorbance ratio
1-blank	0.001	69380	0.000	
2	0.035	68120	0.008	0.229
3	0.156	62380	0.046	0.295
4	0.225	59410	0.067	0.298
5	0.372	53820	0.110	0.296
6	0.539	47950	0.161	0.299
7	0.815	39130	0.249	0.306
8	1.190	30110	0.363	0.305
9	1.602	22290	0.494	0.308
10	2.120	15300	0.657	0.310
11	2.440	11190	0.793	0.325
12	3.020	7730	0.955	0.316
13	4.090	3970	1.246	0.305
14	5.280	1690	1.621	0.307
15	6.570	710	2.010	0.306
16	10.970	59	3.410	
17	13.660	38	4.063	mean
18	15.540	35	4.364	0.300
19	18.410	34	4.540	

Table 2. Comparison of absorbance measurements os starch iodine complex in quartz tubes with the prototype photometer with measurements of the same solutions made in 0.1- or 1-cm cuvettes in the spectrophotometer. Same solutions as in Table 1.

	Sample		
Temp (Deg C)	water	CoCl2	ink
23	70484	31824	32447
37	69206	31626	32202
37	69983	31916	32291
7	69620	33722	32416
7	69598	33612	32466

Table 3. Effects of temperature on the prototype photometer. The optical portion of the photometer and the tubes containing the solutions were equilibrated at the various temperatures for 20 minutes. Duplicate readings taken at 7 and at 37 C.

	Tubes stationary				Tubes at four angles				Tubes spun			
Datum #	1	2	3	4	1	2	3	4	1	2	3	4
Tube #												
1	67016	66938	66896	66825	67144	66814	66626	66348	66377	66647	66680	66713
2	57133	57093	57023	57085	58460	59190	58724	59017	58355	58385	58498	58410
3	48723	48629	48695	48753	48357	48666	48758	48569	47570	47973	47512	47697
4	40751	40656	40656	40785	39282	40007	41787	40285	39996	40153	39940	40052
5	37775	37725	37776	37758	38328	37848	34886	37635	37830	37932	37745	37785
6	27374	27293	27358	27366	27539	26914	27978	27512	27606	27505	27705	27657
7	25313	25305	25314	25348	24930	24372	24651	25394	24779	24992	25025	24966
8	23212	23213	23253	23251	22936	23185	22983	23531	23033	23040	23031	23040
9	24249	24290	24209	24198	24404	24455	24709	23098	24591	24893	24502	24427

Table 4. Effects of spinning tubes during photometry. Frequency data (not converted to absorbances) from nine tubes irradiated with graded doses of UV. All data are from the prototype photometer. The tubes were not moved between measurements in the "Tubes stationary" group, they were set at four different angles in the "Tubes at four angles" block, and were spun during photometry in the "Tubes spun" block.

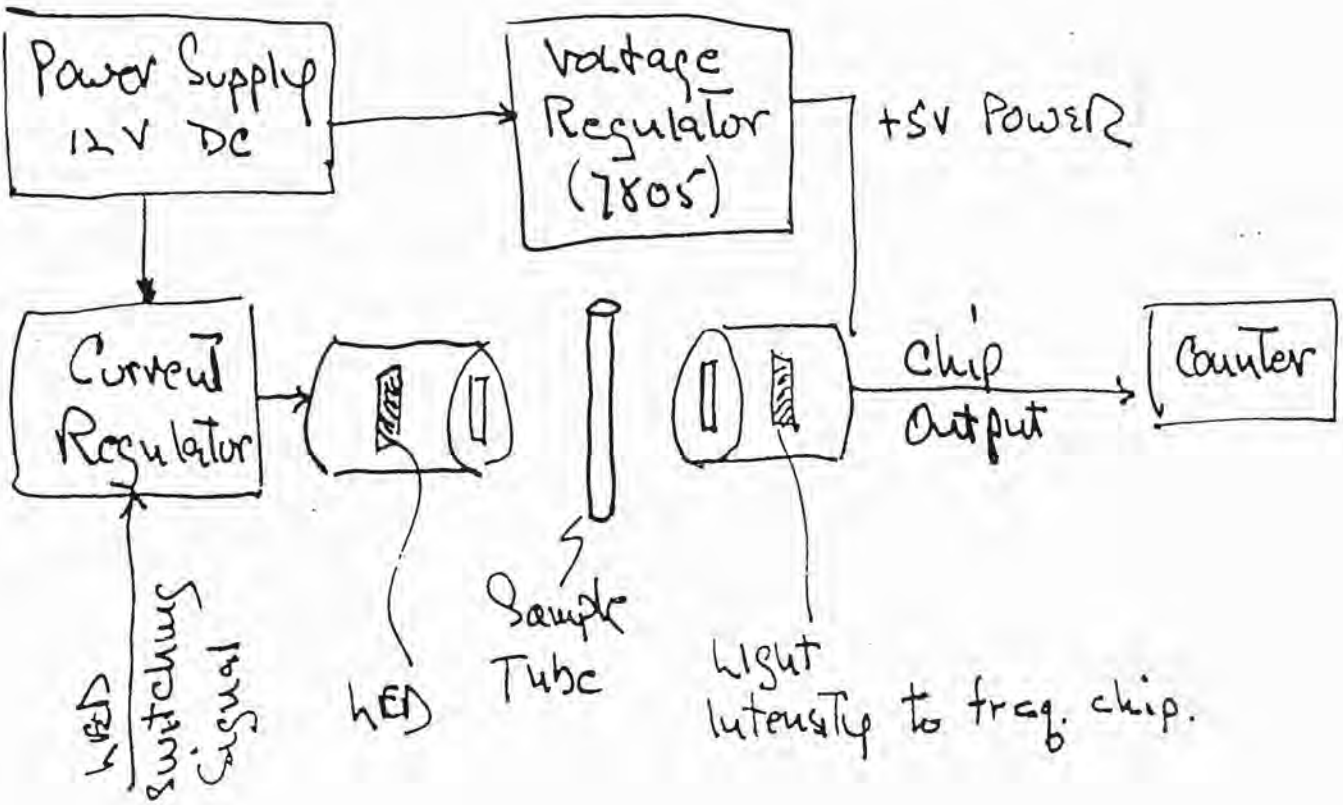

Figure 1. Schematic of Photometer: overview

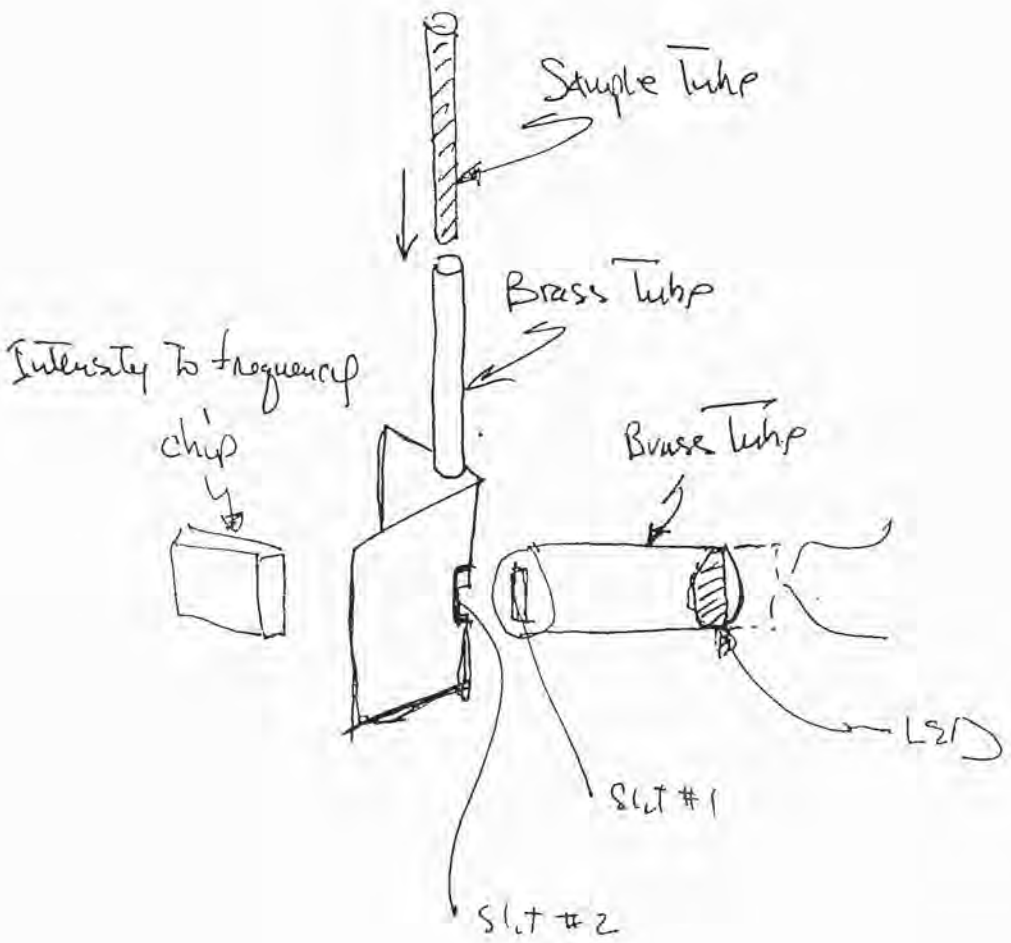

Figure 2. Diagram of Optical Unit of Photometer

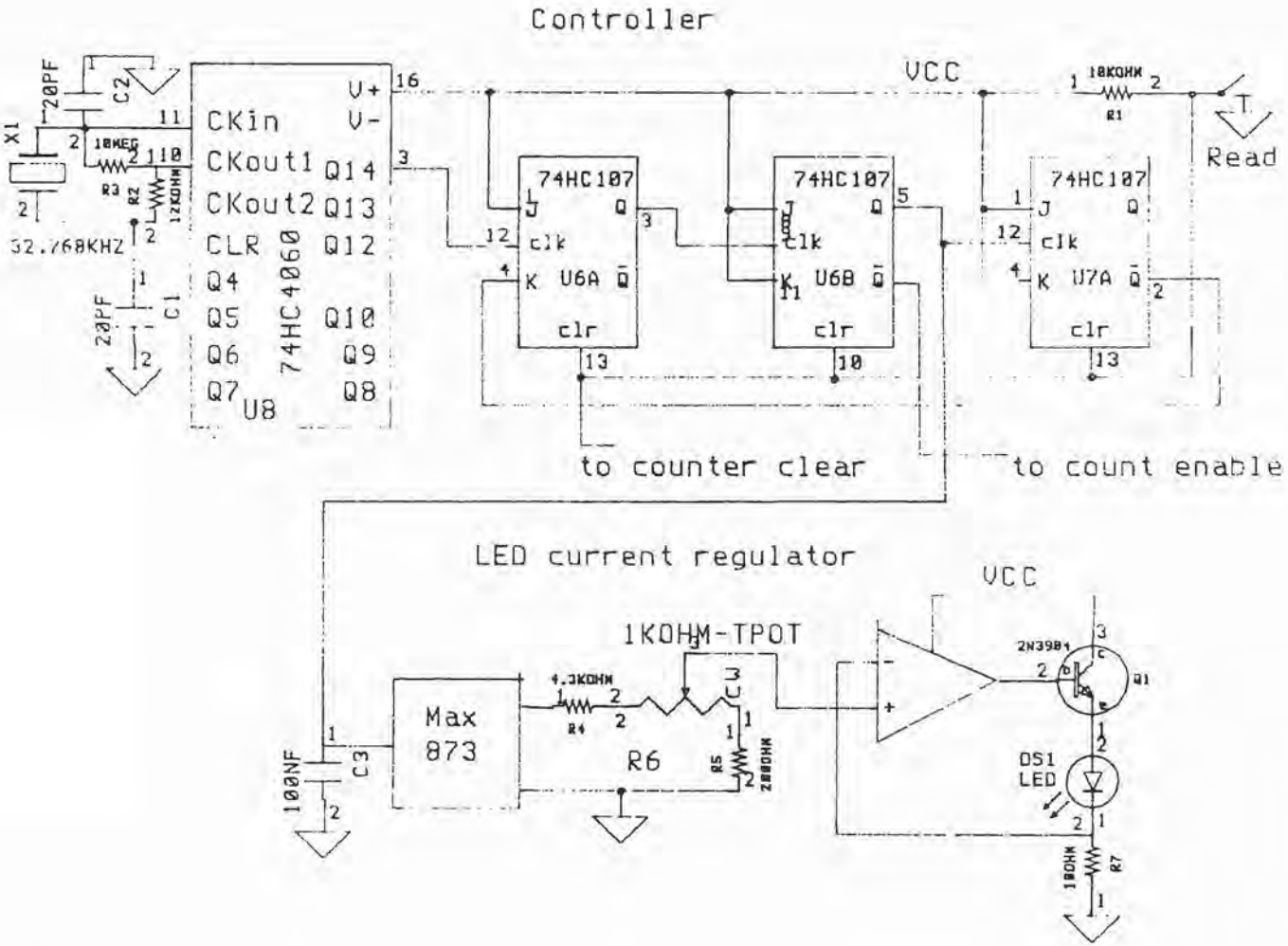

Figure 3. Schematic of Controller

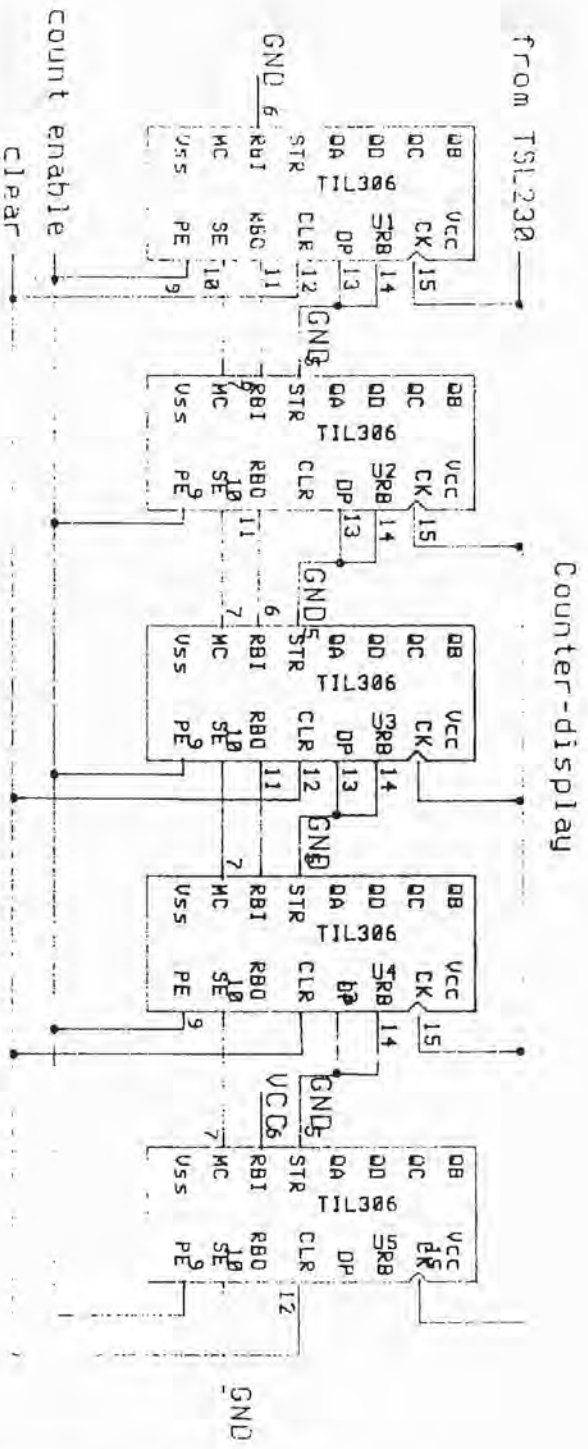

Figure 4. Schematic of Counter/Readout

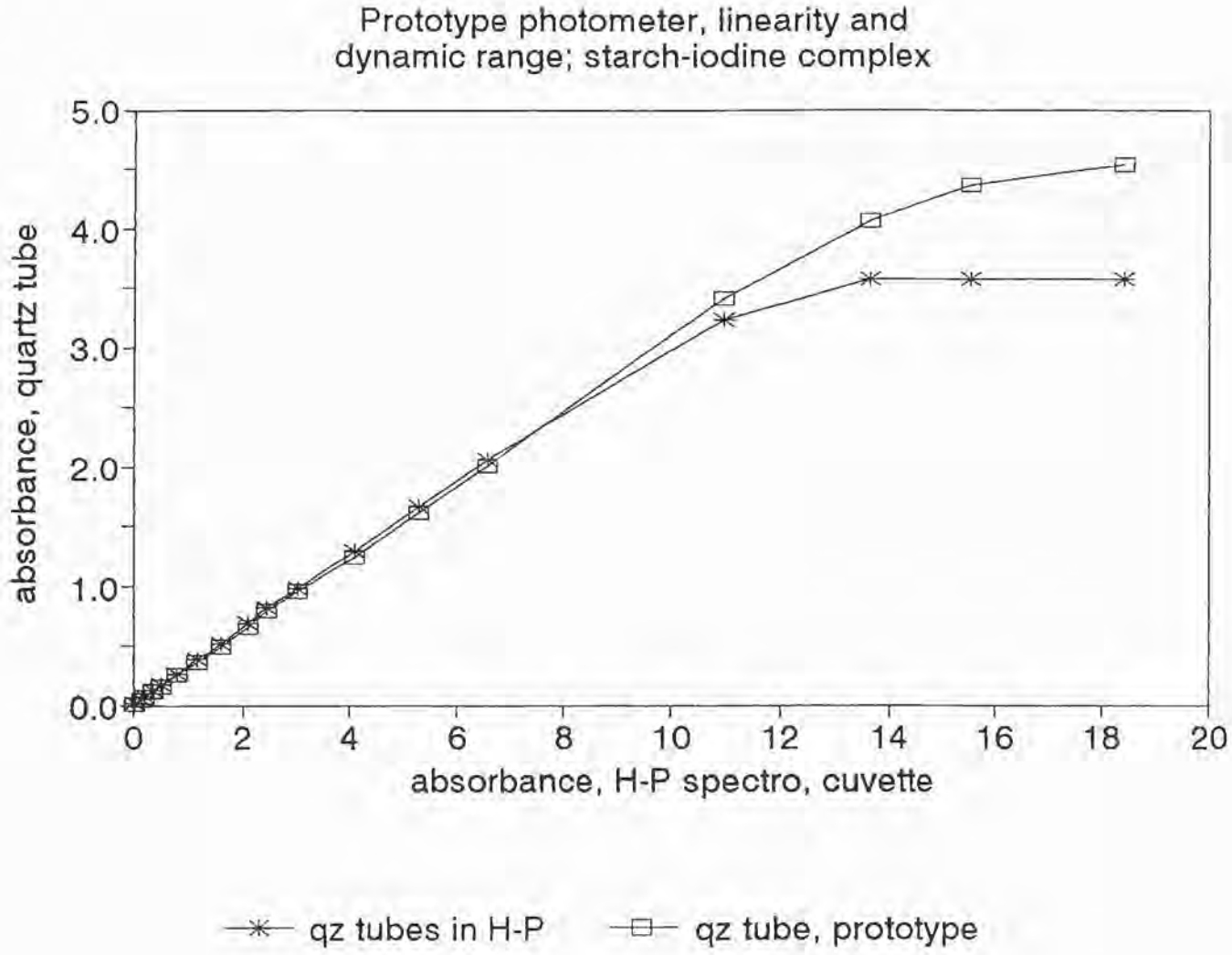

Figure 5. Absorbance as measured in quartz tubes: comparison of spectrophotometer with prototype photometer readings. Data plotted as a function of the absorbance measured in 1-cm cells in spectrophotometer

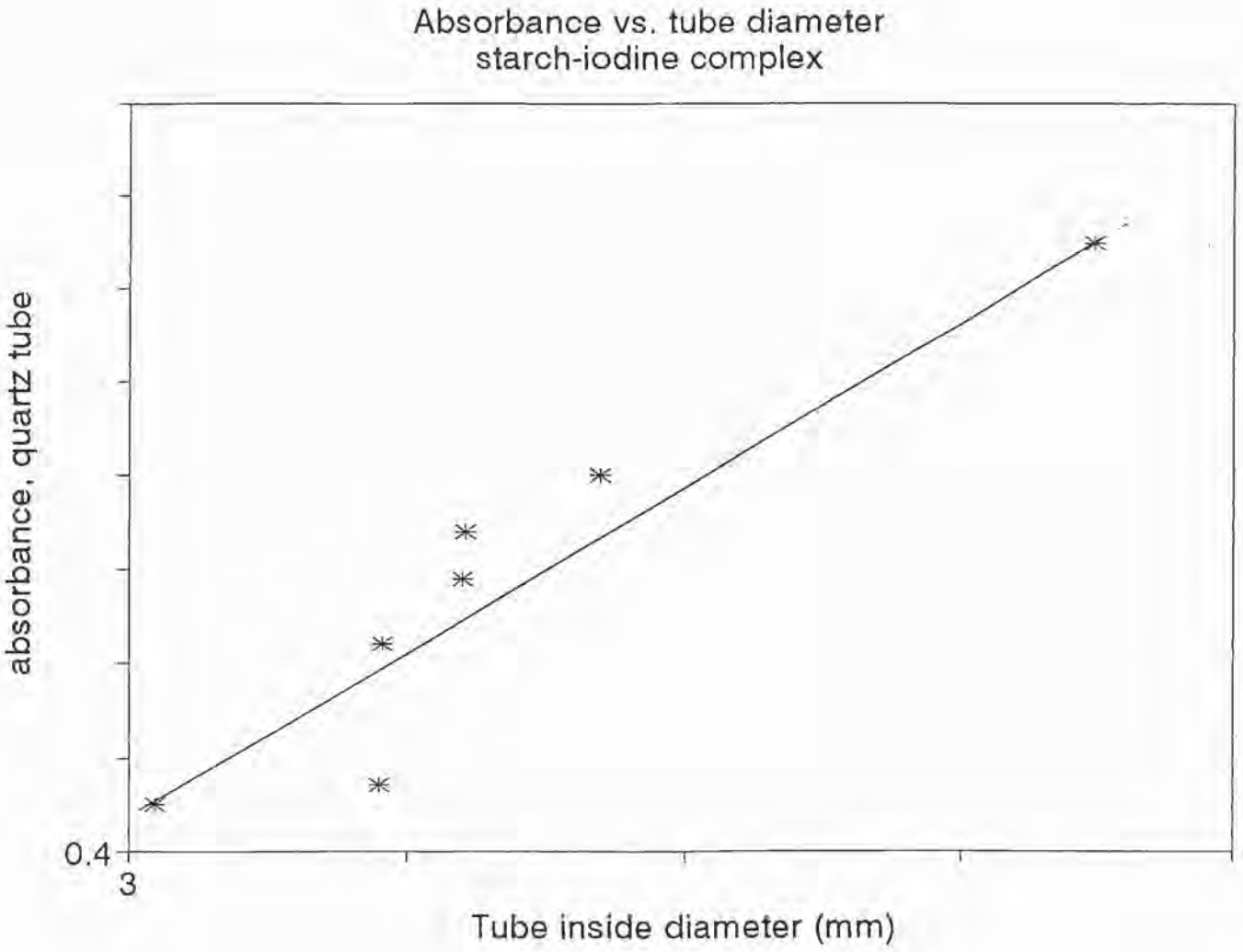

Figure 6. Dependence of absorbance on tube diameter. Measurements made with photometer on same solution in tubes of various sizes.

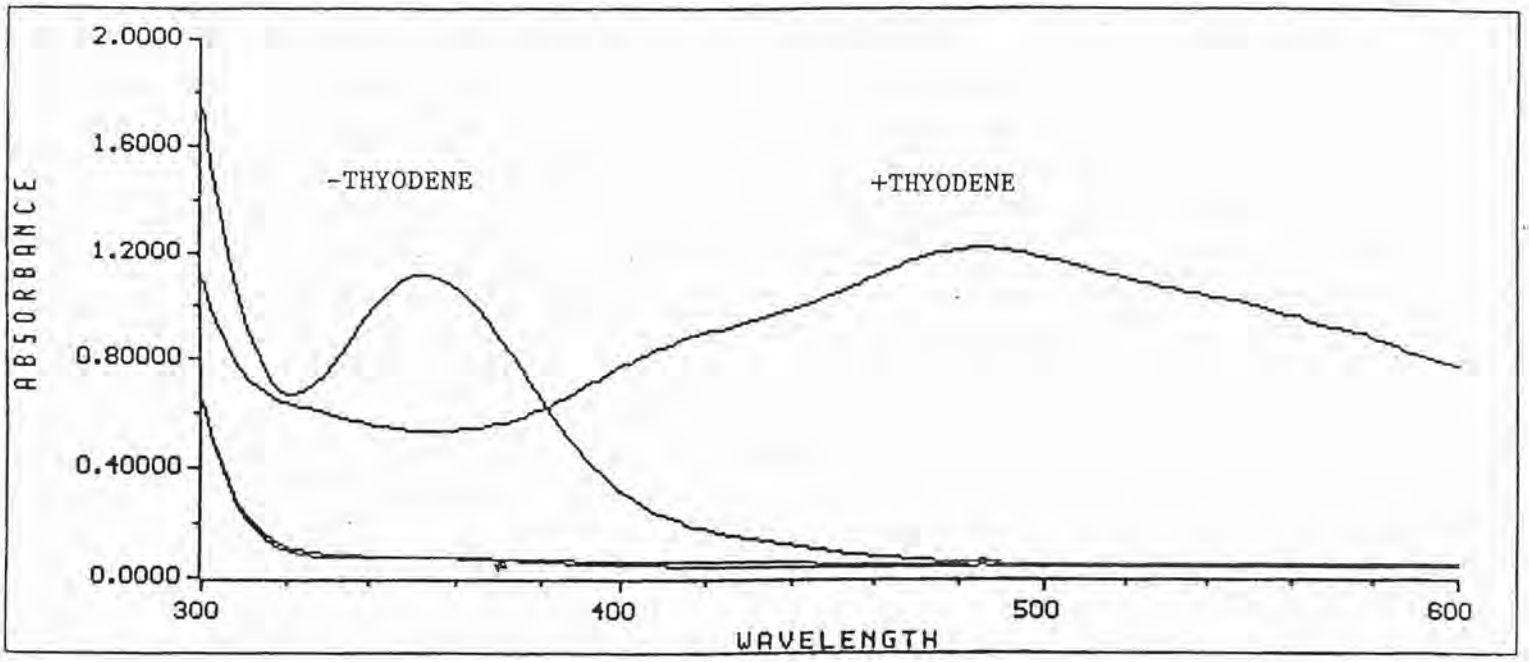

Figure 7. Absorption spectrum of triiodide in the presence and absence of thyodene as measured with a spectrophotometer.

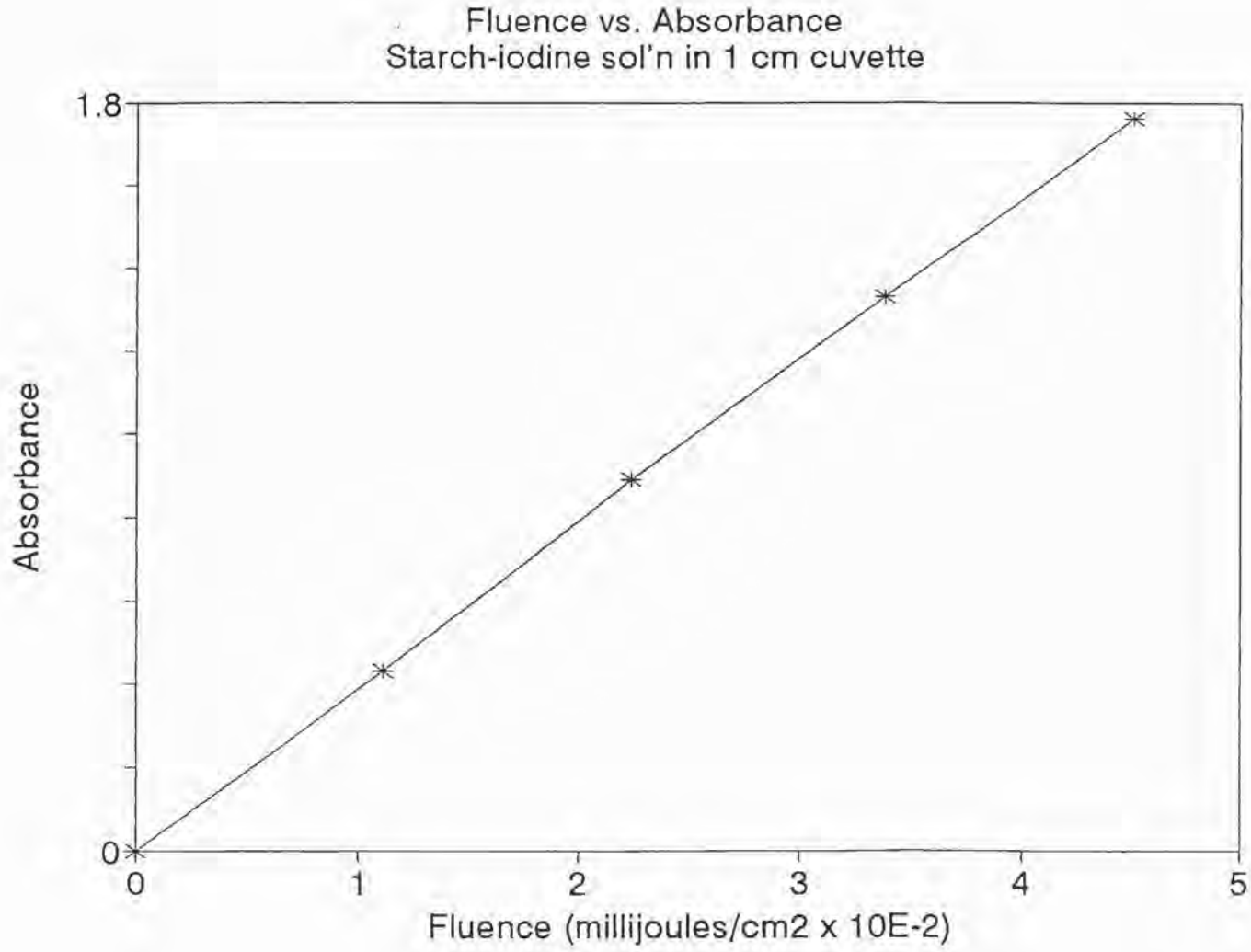

Figure 8. Dose response curve for iodide/iodate actinometric solution following irradiation with low pressure mercury lamp. Irradiation done on solution in 1-cm cell and absorbance measured in spectrophotometer at 470 nm. Concentration of thyodene was 15 mg/ml. Fluence measured with radiometer.

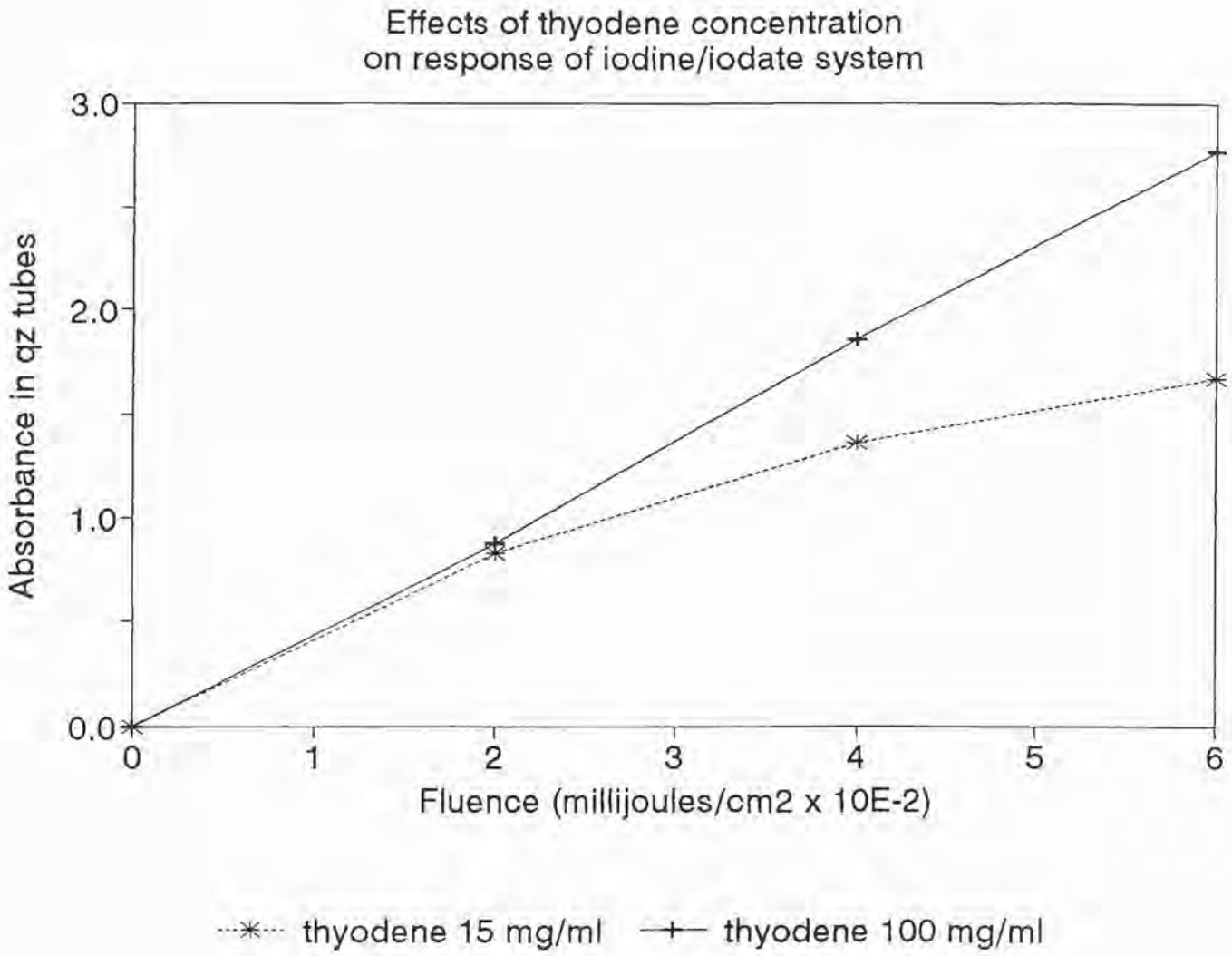

Figure 9. Same as Fig. 8 except samples irradiated in quartz tubes and absorbance measured in photometer. Shown are curves obtained with 15 mg/ml and 100-mg/ml thyodene.

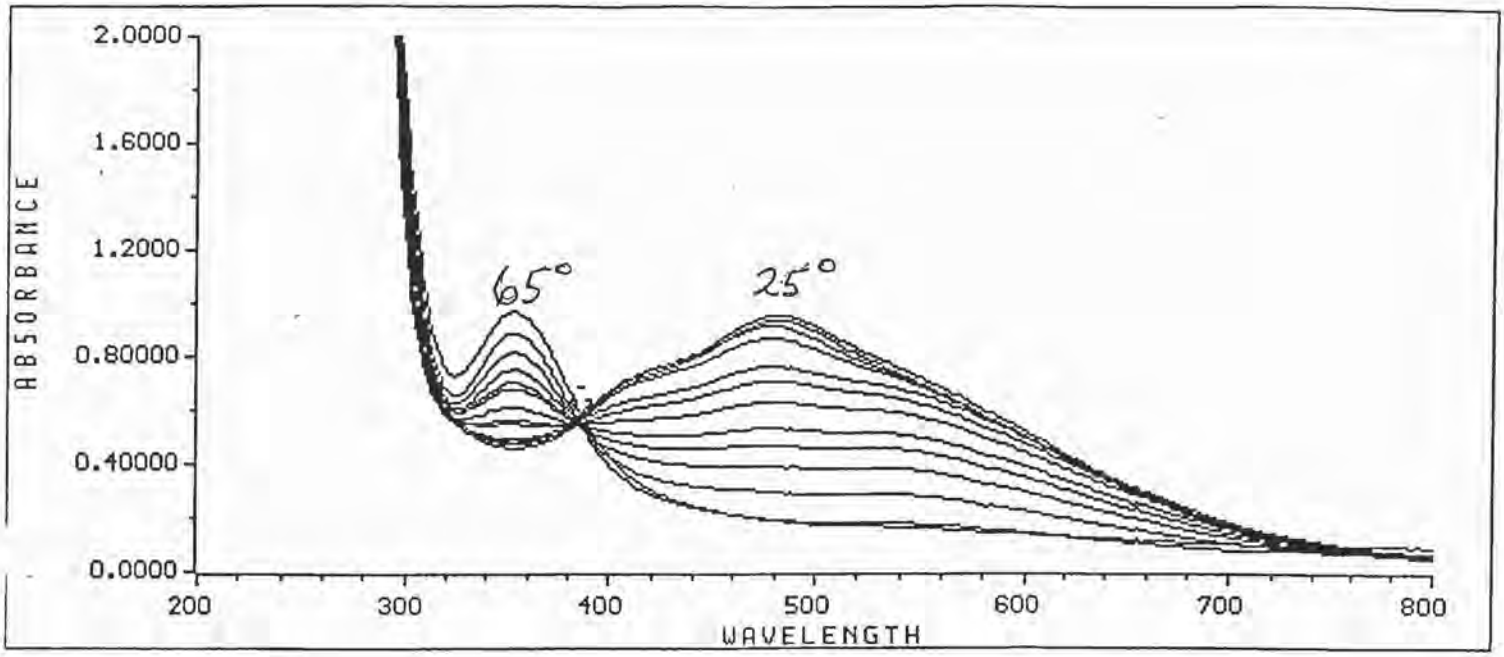

Figure 10. Changes in the absorption spectra of the "starch iodine" complex as a function of temperature. Complex was heated to 65 C and placed in the spectrophotometer where it was allowed to cool to 25 C.

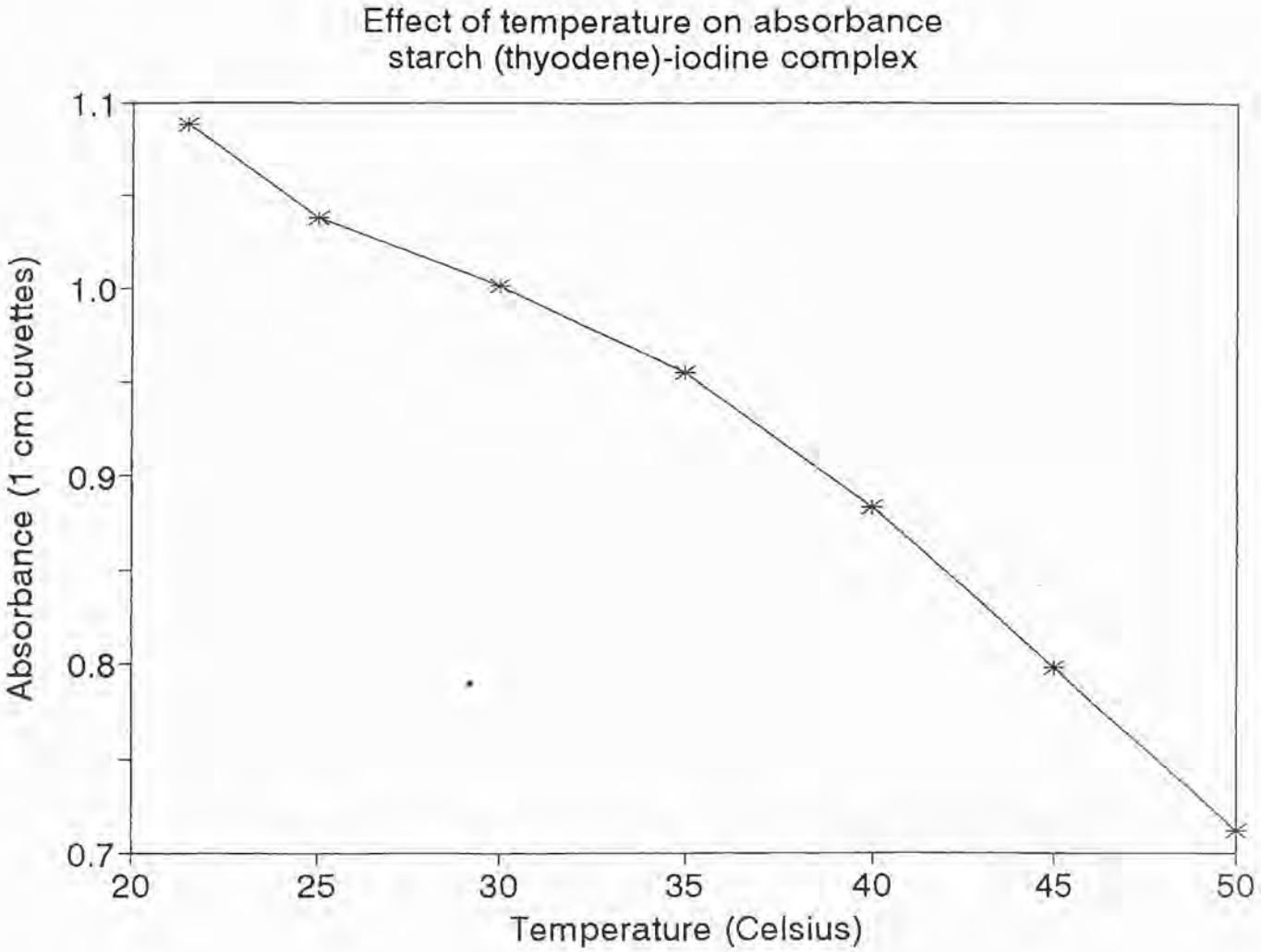

Figure 11 Temperature dependence of absorbance at 470 nm for "starch iodine" complex as measured in spectrophotometer equipped with temperature control unit.

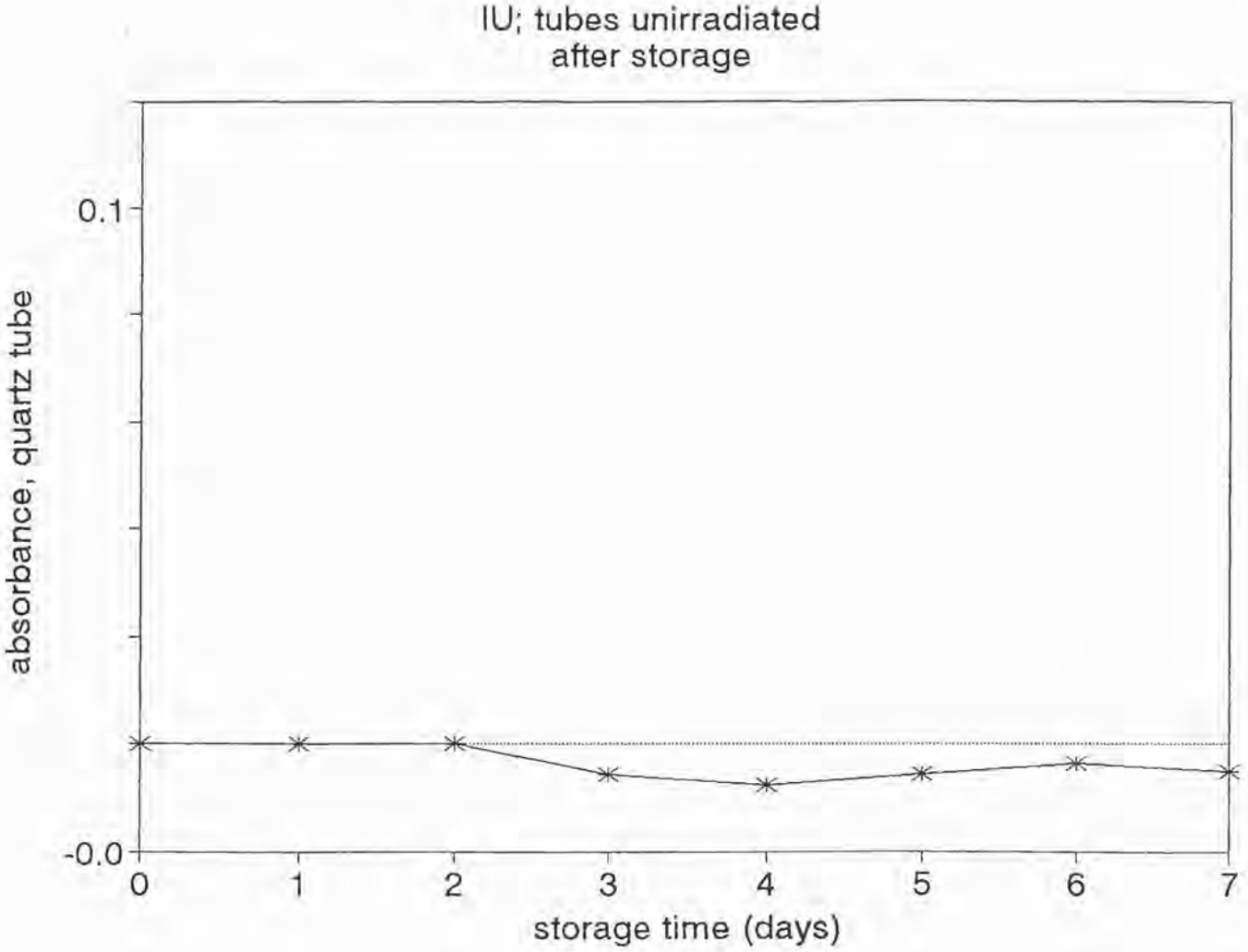

Figure 12 Storage experiment for iodouracil/iodide solutions. Samples stored at either 8 C or room temperature in quartz tubes for various times and then the absorbance measured in photometer.

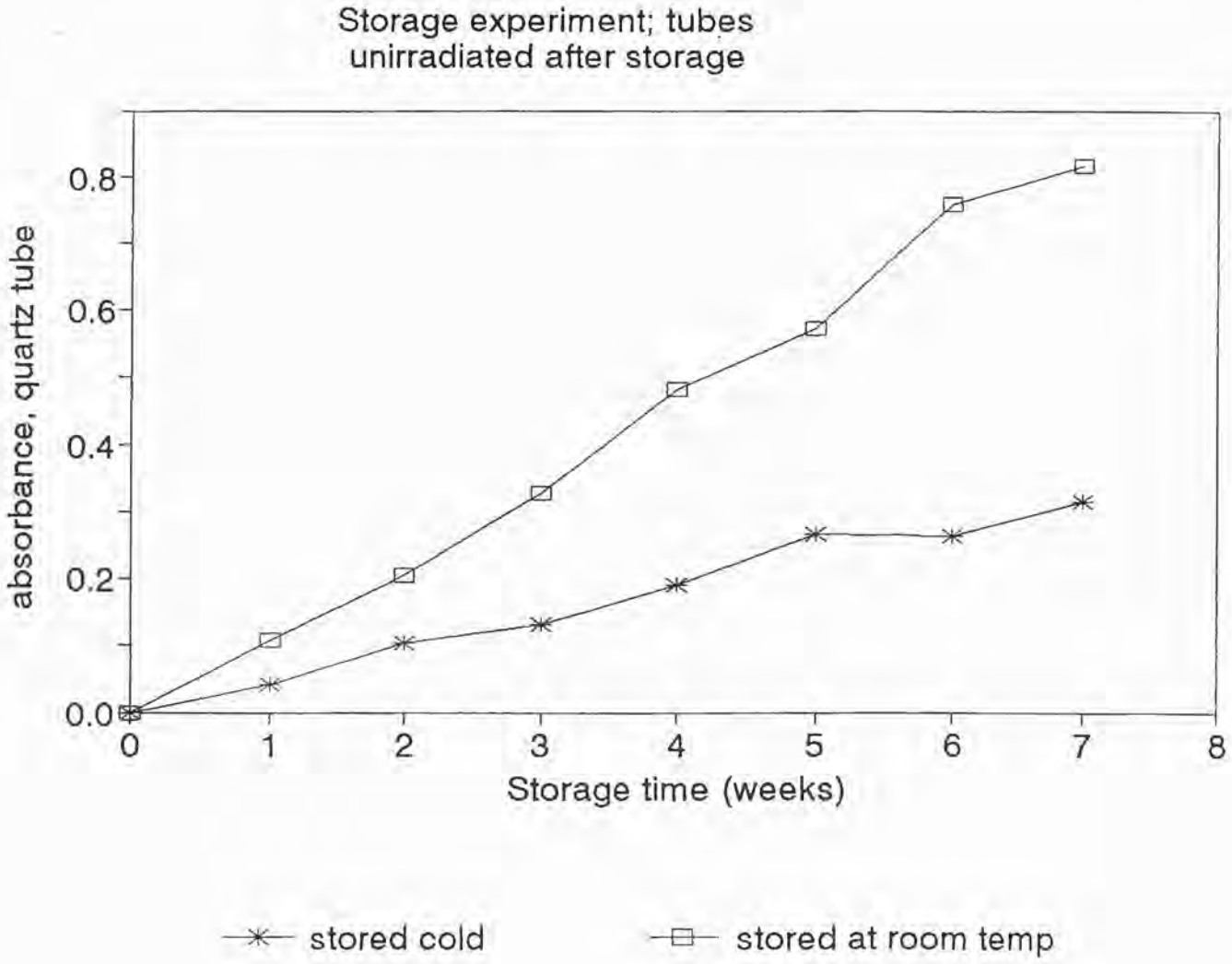

Figure 13 Storage experiment for iodide/iodate solutions stored at either 8 C or room temperature in quartz tubes. Absorbance measured in photometer.

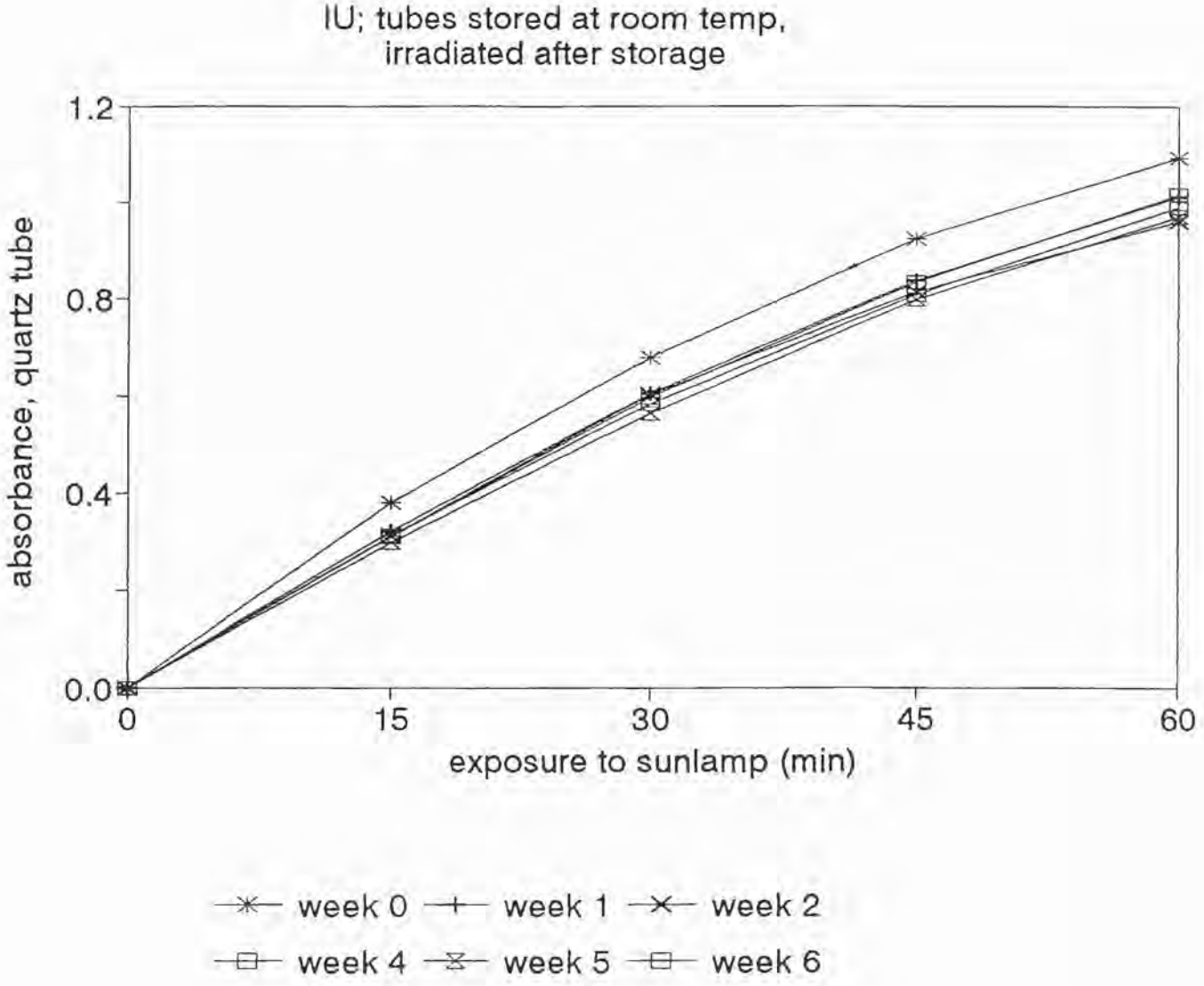

Figure 14 Dose response curves for iodouracil/iodide stored at room temperature for 0, 1, 2, 4, 5, or 6 weeks.

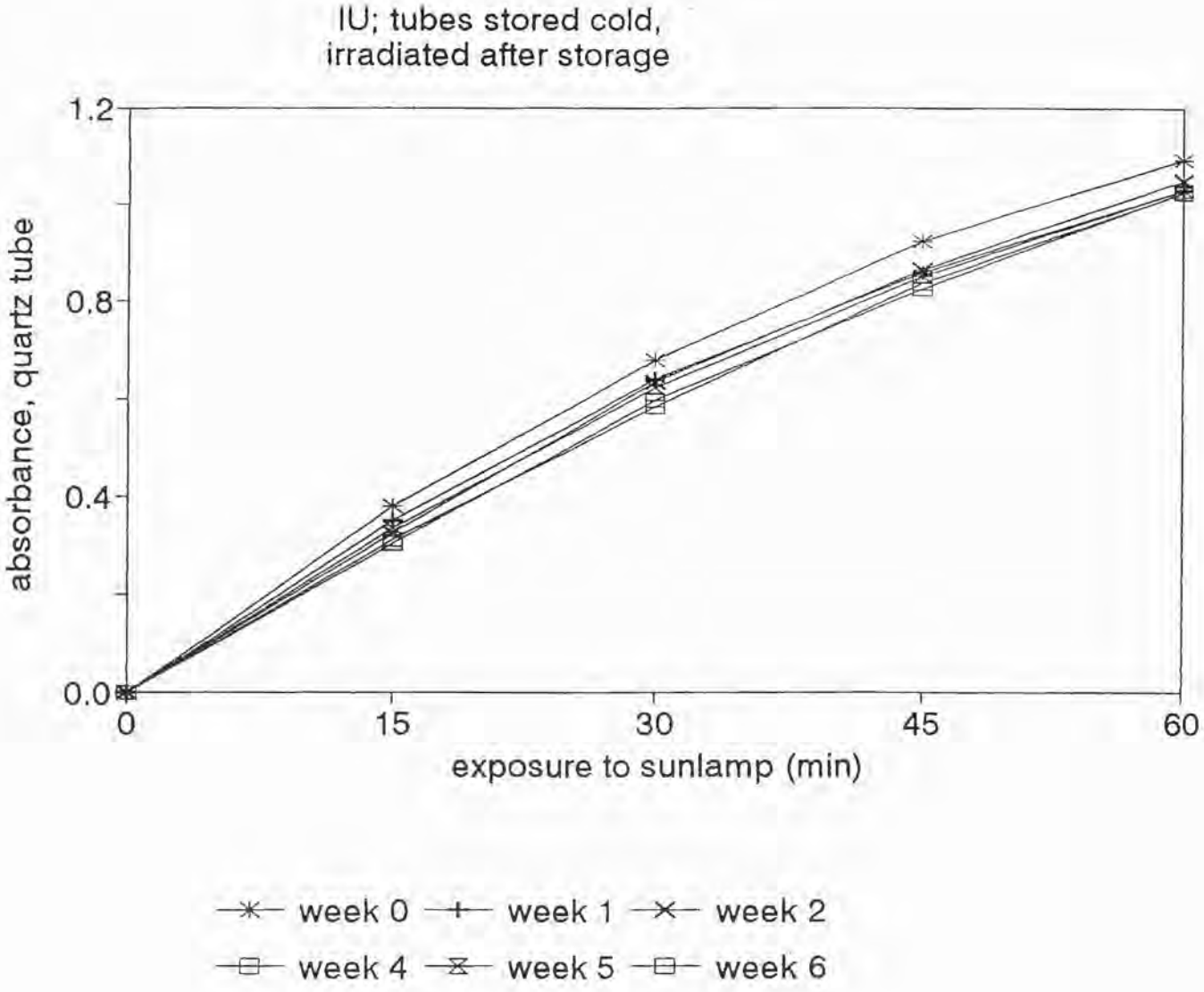

Figure 15 Same as figure 14 except samples stored at 8 C.

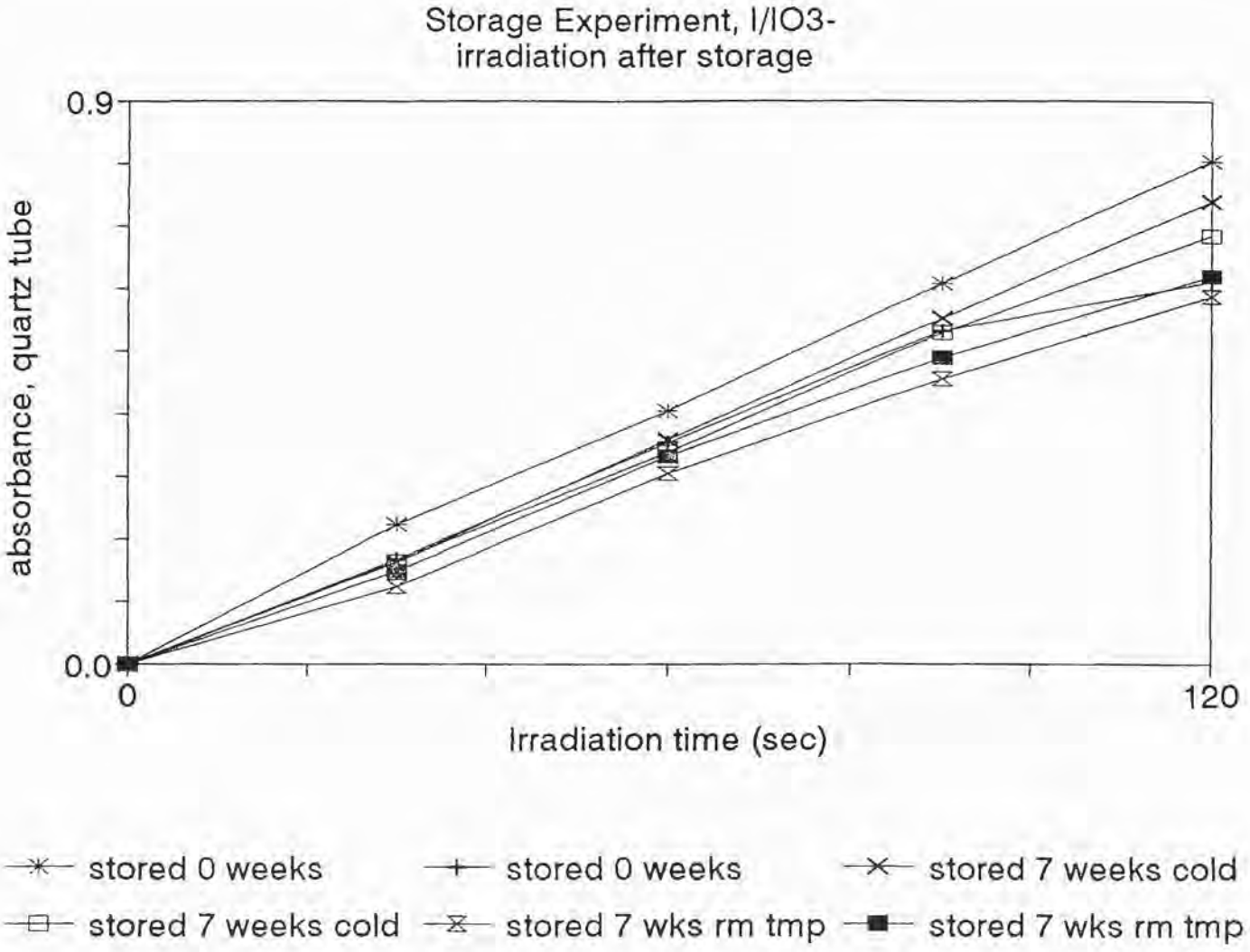

Figure 16. Dose response curves for iodide/iodate samples stored at either 8 C or room temperature for either 0 or 7 weeks.

Acknowledgement

The research reported herein was funded by the Department of Health and Human Services, U.S. Public Health Service SBIR Grant # 1 R43 OH03881-01.

DEPARTMENT OF HEALTH AND HUMAN SERVICES

Public Health Service
Centers for Disease Control
and Prevention (CDC)

Memorandum

Date: April 17, 2001

From: Roy M. Fleming, Sc.D., Director, Research Grants Program RMF
Office of Extramural Programs, NIOSH, D30

Subject: Final Report Submitted for Entry into NTIS for Grant 1 R43 OH003881-01.

To: William D. Bennett
Data Systems Team, Information Resources Branch, EID, NIOSH, P03/C18

The attached final report has been received from the principal investigator on the subject NIOSH grant. If this document is forwarded to the National Technical Information Service, please let us know when a document number is known so that we can inform anyone who inquires about this final report. Five figures are "Proprietary Information"!

Any publications that are included with this report are highlighted on the list below.

Attachment
cc: Sherri Diana, EID, P03/C13

List of Publications None

Title: A Simple Device for Measuring Personal Exposures to UV
Investigator: Stanley D. Echols
Affiliation: Riverbend Instruments, Inc.
City & State: Birmingham, AL
Telephone: (205) 320-1722
Award Number: 1 R43 OH003881-01
Start & End Date: 9/30/1999–6/30/2000
Total Project Cost: $26,250
Program Area: Exposure Assessment Methods
Key Words:

Abstract:
The research was to develop easy-to-use, direct-reading instruments and test kits for measuring exposures rapidly and inexpensively in a variety of workplaces for routine monitoring. This directive, in part, follows from the workplace hazards conference in Chicago in March 1998 sponsored by NIOSH in which non-ionizing radiation was identified as one of the priority areas for further study and research. Development of methodology to aid in the exposure assessment of ultraviolet radiation in the workplace is the goal of the work carried out in this phase I SBIR proposal.

UV exposure or dose can be measured with either an electronic metering device such as a radiometer, or by means of chemical actinometry in which an aqueous solution upon irradiation undergoes a measurable change detected by absorbance or fluorescence. Chemical actinometers which utilize the formation of triiodide as an endpoint are easily measured by absorption spectroscopy. Triiodide can be measured using its absorbance maximum at 352 nm. From this measurement, carried out using 1cm path quartz optical cells for both irradiation and absorbance measurements, the UV fluence can be determined.

In order to develop an inexpensive and portable light-detection device, we decided to use as the light source a light emitting diode (LED). Because LEDs are not available at 352 nm where triiodide absorbs, thyodene, a starch derivative, was used to react with triiodide to form the starch iodine complex, which absorbs strongly at 470 nm, a wavelength at which an LED is commercially available.

The research demonstrated that chemical actinometry using 3 mm ID quartz tubes along with a photometer constructed from a light emitting diode and a light sensitive diode, constitutes an inexpensive, accurate system capable of determining the exposure of workers to ultraviolet hazards. The prototype photometer developed here utilizes recently available light emitting diodes and a light sensitive chip to measure the UV-induced formation of the starch-iodine complex. Individuals in the workplace where UV radiation is present may wear quartz tubes, used to hold the actinometric solutions. The change in the absorbance of the solution due to the formation of triiodide and its reaction with starch can then be monitored using the photometer developed here.

The following objectives were accomplished:

(1) A photometer was constructed with inexpensive components for use with chemical actinometers to permit quantitation of accumulated doses of UV-B and/or UV-C.
(2) The photometer design was optimized for reproducibility and its dynamic range and linear response characteristics determined. Also, the effect of ambient temperature on the instrument response was measured.
(3) The feasibility of using small quartz tubes for long-term storage, radiation exposure and photometric measurements of the actinometric solutions was demonstrated.
(4) Tubes filled with the actinometric solution containing thyodene were irradiated and the absorbance measured in the prototype photometer as a function of the fluence determined using a radiometer. The results were compared with the same solution irradiated in 1-cm quartz cuvettes and measured in a commercial spectrophotometer. These results demonstrate an equivalency between the two methods of measurement. Hence, the prototype system proposed here can be used to determine accurately UV fluence using chemical actinometry.
(5) The effect of temperature on the long-term stability of the actinometric solutions was determined by holding samples of either idode/iodate or iodouracil/iodide at either 8 C or room temperature for up to 7 weeks. Only the iodide/iodate solution showed appreciable formation of triiodide upon storage. The rate of this spontaneous thermal oxidation process was reduced 2-fold at 8 C. The slope of the dose response curves showed at most a small effect of storage, provided background corrections were made.

Publications
No publications to date.