PC 900497

DATA EVALUATION RECORD 2

Yeh, S.M. 1989. R-25788 - Photodegradation in water. Report No. ENV-013. Unpublished study performed and submitted by ICI Americas Inc., Richmond, CA. MRID# 415614-10

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the photodegradation of carbonyl-labeled [^{14}C]R-25788 in aqueous buffer pH 7 solution. No additional information on the photodegradation of R-25788 in aqueous buffered solution is required at this time.

2. R-25788 did not degrade in sterile aqueous buffer solutions (pH 7) that were continuously irradiated with a xenon light source at 25 C for 329 hours.

METHODOLOGY:

Carbonyl-labeled [^{14}C]R-25788 (2,2-dichloro-N,N-di-2-propenylacetamide; radiochemical purity 99.5%, specific activity 25 mCi/mMol, ICI Americas), dissolved in methanol, was added at 46.8 ppm to a sterile aqueous 0.01 M phosphate buffer solution adjusted to pH 7; the final concentration of the methanol cosolvent was 0.4% by volume. Aliquots (8.5 mL) of the treated solution were transferred into sterilized test tubes that each graded from quartz (10-mm id) to Pyrex (3-mm id). The tubes were flame-sealed, and thirteen were placed inside a stainless steel chamber covered with a quartz window (Figure 3). These tubes were continuously irradiated using a UV-filtered xenon arc lamp (Heraeus Suntest) with an emission spectrum between 300 and 800 nm, and a measured average

III. RESULTS AND DISCUSSION

The results of the extraction recovery tests are summarized in Table II. As the data indicate, the recovery was quantitative at each pH tested.

The results of the hydrolysis tests at 25°C at pH 5, 7, and 9 are given in Table III. As the data show, no detectable loss of R-25788 occurred during the 30-day test period. Therefore R-25788 is stable to hydrolysis at 25°C under the test conditions used.

The results of tests at 40°C are listed in Table IV. No losses of R-25788 occurred at pH 5 and 7, indicating stability toward hydrolysis under these conditions. At pH 9 approximately 10% of the starting material disappeared during the test period, suggesting slow hydrolysis. The first-order rate constant and half-life for the hydrolysis reaction were calculated to be 3.8×10^{-3} day^{-1} and 185 days, respectively.

intensity of 492 W/m^2; it was stated that 12.8 days of continuous irradiation with the xenon lamp was equivalent to 30 days of summer sunlight in Richmond, CA (Figures 1 and 2). The temperature of the tubes was monitored using a thermocouple, and was maintained at 23.6-25.7 C by a recirculating waterbath surrounding the photoreactor. For a dark control, six additional tubes of the treated solution were wrapped in aluminum foil, then placed in a separate, constant-temperature water bath at 25 C. Duplicate tubes of irradiated solution were collected for analysis at 0, 24, 96, 142, 190, and 262 hours posttreatment; three tubes were collected at 329 hours. Single tubes of the dark controls were collected at 0, 96, 142, 262, and 329 hours posttreatment.

At each sampling interval, aliquots of each sample were analyzed for total radioactivity using LSC. Additional aliquots were analyzed for R-25788 and its degradates by HPLC using a C-18 ODS2 phase-separation column with a Brownlee OD-GU guard column eluted with methanol:water (50:50, v:v), with radiochemical and UV (220 nm) detection; HPLC fractions were quantitated by LSC. Aliquots from two of the three irradiated solutions collected at the 329-hour sampling interval were combined and extracted with methylene chloride; aliquots of the extract and the extracted aqueous solution were analyzed by LSC. The remainder of the extract was characterized by GC/MS.

DATA SUMMARY:

Carbonyl-labeled [^{14}C]R-25788 (2,2-dichloro-N,N-di-2-propenylacetamide; radiochemical purity 99.5%), at 46.8 ppm, did not degrade in sterile aqueous buffer solutions (pH 7) that were continuously irradiated at approximately 25 C for 329 hours using a UV-filtered xenon arc lamp with an emission spectrum and a measured average intensity (492 W/m^2) that approximated sunlight during the summer in Richmond, CA (Table I).

At all sampling intervals, R-25788 accounted for ≥97.5% of the radioactivity recovered from both the irradiated samples and dark controls (Table I). Also, the 329-hour methylene chloride extract was determined by GC/MS to contain only R-25788. Material balances were ≥100% of the applied during the study.

COMMENTS:

1. Temperature measurements within the photoreactor were made three times daily. Average daily temperatures ranged from 24.5 to 25.3 C; measured temperatures ranged from 23.6 to 25.7 C.

2. The dark control sample cell retrieved on the final day of the study (329 hours) was cracked by accidental freezing prior to LSC analysis. Although attempts were made to contain all of the frozen solution, only 88% of the applied radioactivity was recovered.

3. The adsorption spectrum of R-25788 in water (pH 7) was presented in Figure 6.

TABLE I

Material Balance by LSC of Test Solution Aliquots and R-25788 Quantitation by LSC of HPLC Fractions

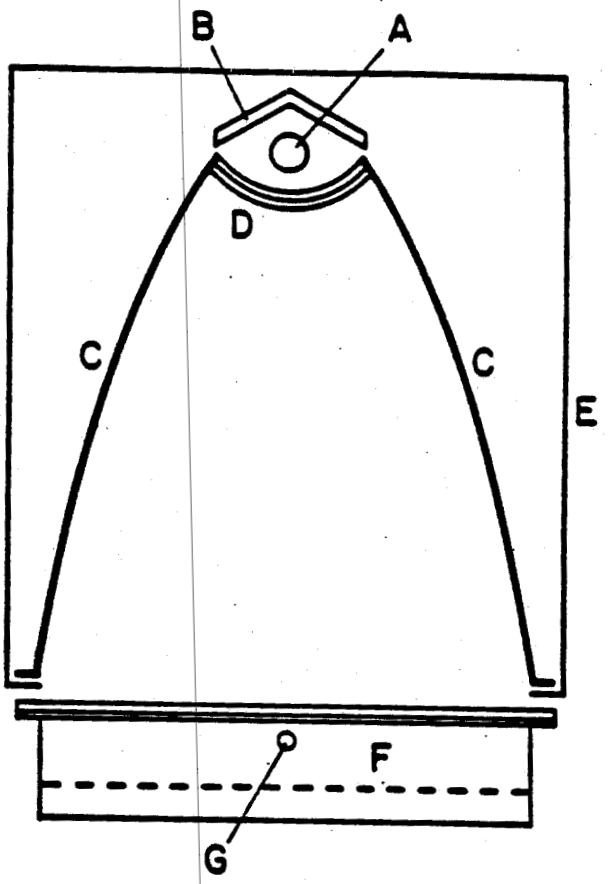
Sample	WRC Code 11794-16	Hours of Light	% Material Balance*	HPLC Fraction Percent Total for Fractions 2-6 min % ^{14}C	HPLC Fraction Percent Total for R-25788 12-16 min % ^{14}C
4/13A	- 1	0	102	0.3	98.8
4/13B	- 2	0	101	0.2	98.6
4/14A	- 3	24	102	1.1	98.0
4/14B	- 4	24	100	0.5	98.6
4/17A	- 6	96	102	0.6	98.8
4/17B	- 7	96	100	0.6	98.1
4/19A	- 9	142	103	0.6	98.6
4/19B	-10	142	101	0.7	97.6
4/21A	-12	190	100	0.8	98.6
4/21B	-13	190	101	0.9	97.9
4/24A	-15	262	102	0.8	98.4
4/24B	-16	262	100	1.0	97.8
4/27A	-18	329	102	1.1	97.5
4/27B	-19	329	101	1.0	98.1
4/27C	-20	329	100	1.0	98.2
DARK CONTROLS					
4/17	- 8	0	101	0.5	99.0
4/19	-11	0	101	0.5	98.8
4/24	-17	0	101	0.4	98.7
4/27	-21	0	88.2**	0.5	99.0

*average material balance = 101% (± 1%), excluding the 4/27 dark control, see footnote **.

**The sample cell was cracked by accidental freezing in the refrigerator. The frozen solution had to be melted in a larger container; the slightly lower value may be due to loss from volatilization during the melting process.

Figure 1

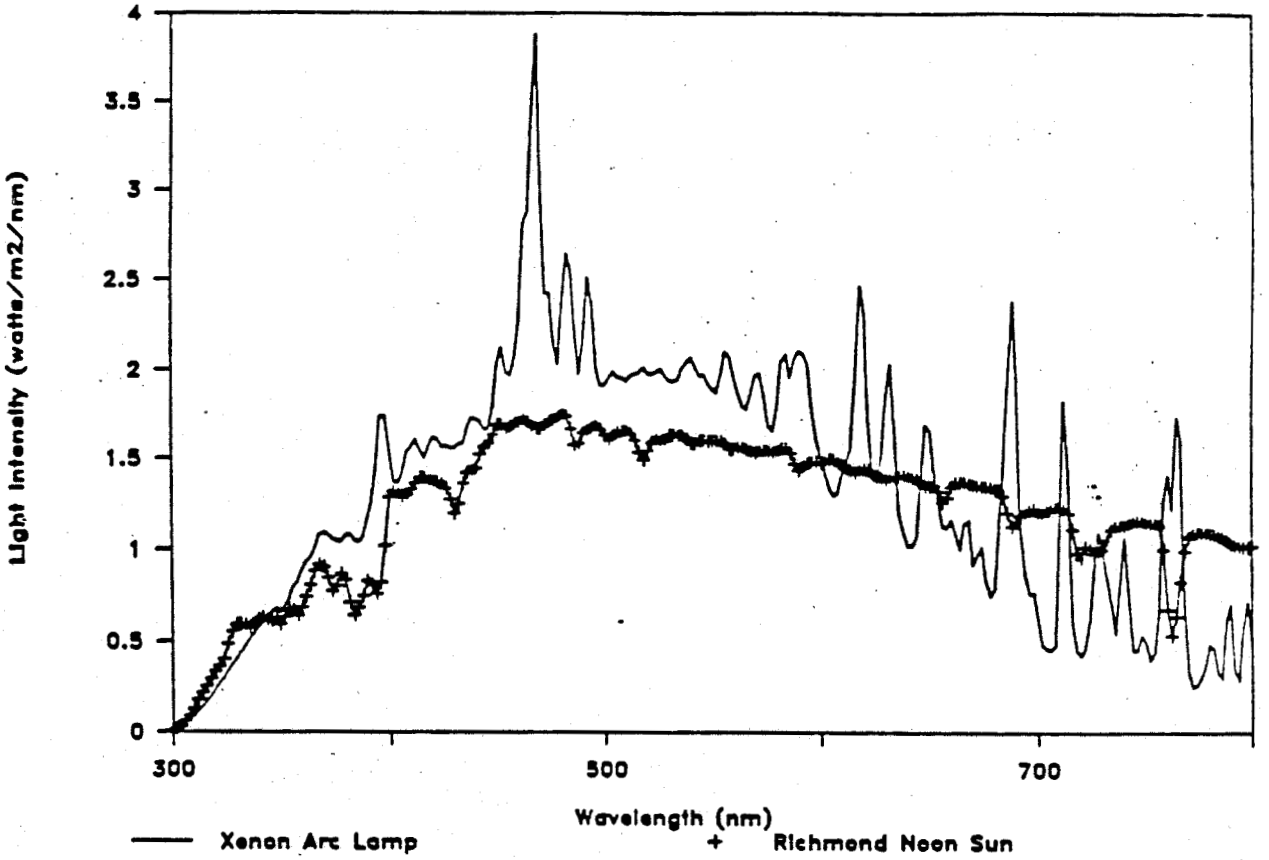
Xenon Arc Lamp Schematic
Artificial Light Source



A Xenon Arc Lamp
B Ultraviolet Mirror (Transmits IR)
C Parabolic Mirror
D Filters
E Protective Housing
F Sample Chamber (see Fig. 1)
G Air Inlet

Figure 2

Comparison of Xenon Arc[1] and Solar[2] Spectral Distributions[3]



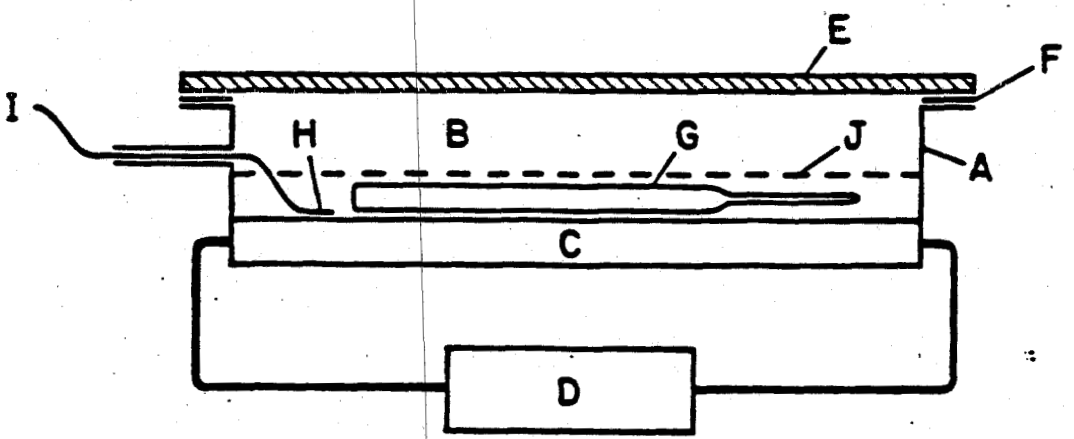
1. The spectrum of the xenon arc lamp (Heraeus Suntest) was taken on May 25, 1988, at the same distance from the lamp that photolysis samples would be placed.

2. The solar spectrum was taken in Richmond CA at 1:08 pm on June 21, 1988 (cloudless conditions).

3. Both spectra taken with a LI-COR model No. LI-1800/12 UV/visible spectroradiometer.

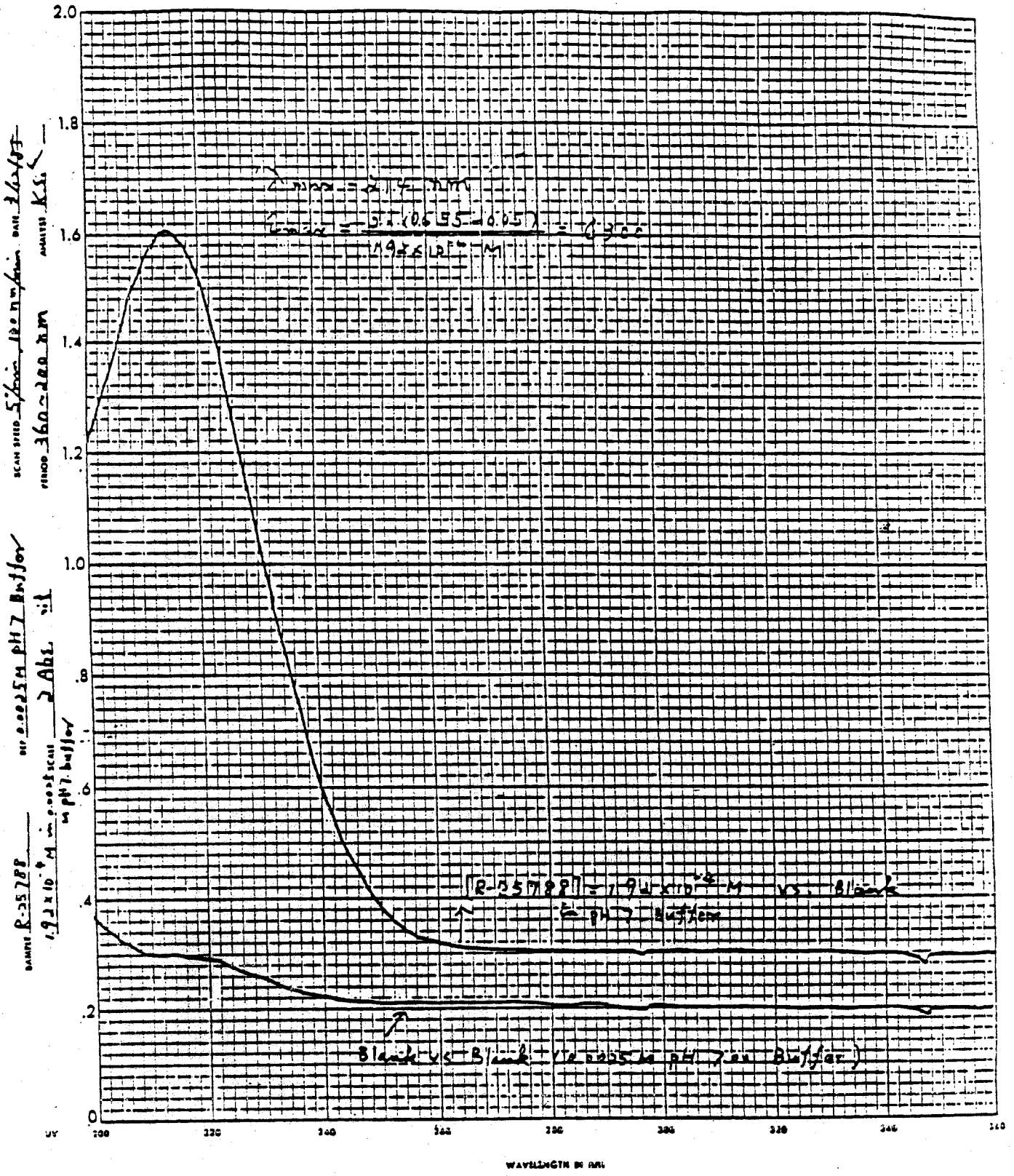
Figure 3

Photoreactor Schematic



A. Stainless Steel Chamber
B. Sample Compartment
C. Coolant Compartment
D. Recirculating Constant Temperature Bath
E. Quartz Plate
F. PTFE Gasket
G. Sealed Quartz Sample Tubes
H. Thermocouple
I. Thermocouple Lead
J. Water

Figure 6



UV Spectrum of R-25788, Solvent = Water at pH 7.

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

IV. RESULTS AND DISCUSSION.

A. Overview

The starting material was characterized by GC/^{14}C detection, TLC/^{14}C detection, GC/MS, and NMR. Its radiopurity was > 99%. Aqueous solutions of R-25788 were exposed to light from a xenon arc lamp for up to 329 hours; seven time points were examined, including the zero time sample. GC/MS analysis of a dichloromethane extract from the final photolysis sampling point confirmed the presence of parent R-25788 and the absence of photodegradation products. This dichloromethane extraction removed over 97% of the total radioactivity from the aqueous sample. At each sampling time, HPLC/^{14}C detection was used to monitor the replicate samples; the only peak detected on the radiochromatogram was the parent R-25788. Fractions from the HPLC runs were also collected and quantitated by LSC.

B. Product Identification

The dichloromethane extract from the final photolysis time point was determined by GC/MS to contain only intact R-25788. The GC/MS analysis showed only one peak, which gave the correct EI mass spectrum for R-25788 (Ref. Spectrum No. 250571; see Fig. 4).

Each treated sample was analyzed by HPLC with on-line ^{14}C detection, UV detection, and LSC of collected fractions. When unlabeled R-25788 standard was spiked into a portion of the t = 329 hour photolyzed solution, it co-eluted (as measured by UV detection) with the peak assigned to R-25788 in the photolyzed sample (see Fig. 5).

Table II lists the retention times (UV) of R-25788 and four other standards. Sample HPLC chromatograms are given in Fig. 5. The delay time between the UV detector and the radioactivity detector was approximately 0.5 minutes. Typically, the fractions were collected every 2 minutes, after an initial pause of 48 seconds at the beginning of each HPLC run.

C. Product Quantitation

The radioactivity in the chromatographic runs was quantitated by both an on-line radiochemical detector as well as off-line liquid scintillation counting of collected fractions. Because the R-25788 peak was the only one observed on the radiochromatograms and because integration showed that R-25788 constituted essentially 100% of the total of peak areas, only the information from the fractions was used to determine the amounts of intact R-25788. The values for R-25788 (from LSC analysis of fractions from individual HPLC runs) ranged between 97.6% and 98.8% throughout the course of the photolysis experiment (see the last column on the right in Table I).

D. Material Balance

The material balance at all time points was good, averaging 101% and ranging between 100 and 103%. The material balance values at the different time points are given in the material balance column of Table I (see Appendix 3 for calculations and raw data).

E. Temperature Measurements

The average temperature over the course of the experiment was 24.9° + 0.4°C (±1 standard deviation), judging from the average of three daily measurements over the course of the experiment. The temperatures ranged from a low of 23.6°C to a high of 25.7°C.

F. Photolysis Rate

The pseudo first-order photolysis half-life and rate constant were not calculated because photolytic degradation, if any, was less than 1% of the total radioactivity present in the photolyzed samples.

The absence of observable photolytic degradation was consistent with the absorption spectrum of R-25788 in aqueous solution, shown in Fig. 6. The absorption maximum was at 214 nm, and virtually no absorption occurred at wavelengths greater than 270 nm. Thus, there were no strong electronic transitions for interaction with light under the conditions of this experiment, i.e., light of wavelengths $\geq$ 290 nm.

V. CONCLUSIONS

Measurable aqueous photolysis of R-25788 did not occur at 25°C and pH 7 after continuous exposure to a xenon lamp for 13.7 days, the equivalent of 32 days of natural summer sunlight at latititude 37° 56' N.