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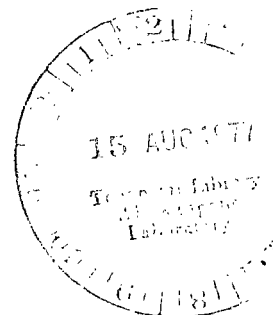


**REMOTELY SENSED AND
LABORATORY SPECTRAL SIGNATURES
OF AN OCEAN-DUMPED ACID WASTE**

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REMOTELY SENSED AND LABORATORY SPECTRAL SIGNATURES

OF AN OCEAN-DUMPED ACID WASTE

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SUMMARY

An ocean-dumped acid waste plume was studied by using a rapid scanning spectrometer to remotely measure ocean radiance from a helicopter. The results of these studies are presented and compared with results from sea-truth samples and laboratory experiments. An ocean spectral reflectance signature and a laboratory spectral transmission signature were established for the iron-acid waste pollutant. The spectrally and chemically significant component of the acid waste pollutant was determined to be ferric iron.

The remotely sensed ocean spectral reflectance of the plume and the laboratory spectral transmissivity as a function of iron concentration are used to estimate the concentration of the acid waste in the plume by means of a simple mathematical model. The method compares the shape (color) of the spectral reflectance curves, calculated for various iron concentrations from laboratory transmissivity data, with the remotely measured spectral radiance curves of the plume. The calculated curve which most nearly matches the shape (color) of the plume curve gives the estimated concentration of iron in the plume at the point of measurement. In the limited number of stations where good remote spectral data were obtained, the agreement with sea-truth iron concentration was quite good. These studies indicate that remotely sensed monitoring of acid waste is feasible.

INTRODUCTION

Ocean dumping of acid wastes and sewage sludges has been practiced under permit for several years with only a minimum of information as to the ecological or environmental impact (refs. 1 and 2). Growing concern by the Environmental Protection Agency and the National Oceanographic and Atmospheric Administration over the consequences of ocean dumping in general has resulted in studies to determine what the impact may be and to devise means for monitoring such dump areas. Acid waste dump plumes have been seen in remotely sensed imagery from both satellite and aircraft (refs. 3 and 4). Little has been done to define the spectral signature of acid waste in ocean water or to relate color changes upon dilution and dispersion to acid waste concentrations. This information is necessary to be able to identify and monitor acid waste dumping by remote-sensing techniques. Information on the chemical interaction of the acid waste with ocean water and its influence on spectral changes is needed to be able to interpret ocean color changes in the dump areas.

In recognition of these needs, Langley Research Center and the College of Marine Studies of the University of Delaware jointly planned a research program to obtain and analyze the information required to define remote-sensing spectral signatures and techniques for monitoring ocean-dumped pollutants. The first pollutant selected for study was the acid waste from a titanium dioxide processing plant at Edgemoor, Delaware. Table I gives the typical chemical composition of this acid waste. The acid waste, which contains relatively large quantities of ferric chloride in a 1 to 2 M hydrochloric acid solution, is regularly dumped at a designated site about 65 km (35 n. mi.) out in the Atlantic Ocean off Cape Henlopen, Delaware. An experiment was planned and conducted jointly by Langley and the University of Delaware (ref. 5) to obtain remote-sensing data, "sea-truth," and laboratory spectral and chemical data for an actual acid waste dump. The dump experiment took place on August 28, 1975, an almost perfect remote-sensing day (clear, bright skies and relatively calm seas). Operational details of the experiment are given in a report by Hypes and Ohlhorst (ref. 5).

Although several remote-sensing instruments obtained data during the test (ref. 5), this report summarizes only those obtained with a rapid scanning spectrometer (RSS) from a helicopter flying at an altitude of 609.6 m (2000 ft) over the sea-truth stations. Sea-truth water samples were taken from a surface vessel stationed nominally in the center of the plume at the same time the helicopter with the RSS was flying over the station.

The results of chemical analysis of the sea-truth water samples and laboratory experiments using the acid waste and ocean water samples obtained during the test are summarized and related to the remotely sensed data.

INSTRUMENTS AND METHODS

Remote Sensing With the RSS

The instrument used to obtain the remotely sensed spectral data (and laboratory data) was the Tektronix rapid scanning spectrometer (RSS). This instrument was chosen because it had the capability of producing a 400-nm spectral radiance curve every 20 msec, was portable, and could be used both in the laboratory and in the field. Figure 1 is a schematic representation of the RSS. In general terms, a spectral image is produced by a grating monochromator on a target vidicon and this image is scanned with an electron beam every 20 msec, producing signals proportional to the spectral radiant energy received by the spectrometer.

During the remote sensing of the acid waste plume at the dump site, a 300-mm lens was used on the RSS to limit the field of view of the ocean water and plume. The sensing head with lens attached was shock mounted in a frame (fig. 2), enclosed in a fiber-glass box, and hung vertically beneath a Bell UH-1B helicopter (fig. 3). To assist in registering the RSS field of view, a 70-mm time-sequenced camera was also mounted beneath the helicopter (fig. 3) and photographs were taken at 15-sec intervals during each data pass over a station.

The RSS remote-sensing data-taking technique used for the acid waste plume is illustrated in figure 4. The RSS, pointed vertically down at the ocean, was flown across the acid waste plume at an altitude of 609.6 m (2000 ft) at the same time the crew of the sea-truth vessel (RV Annandale) was taking water samples and making in situ measurements (ref. 5). Three passes over each station were made so that three different wavelength ranges covering a total range of 300 to 1100 nm could be obtained. The three ranges were 300 to 700, 500 to 900, and 700 to 1100 nm. The range switch on the RSS sensing head was changed between passes.

The electronics, oscilloscope, and tape-recording equipment were inside the helicopter and the data obtained by the sensing head were monitored on the oscilloscope and recorded on tape for computer processing at Langley.

Figure 5 is one of the photographs taken during a data pass, showing the sea-truth vessel on station in the acid plume. At an altitude of 609.6 m (2000 ft), the instantaneous RSS field of view was 14.02 m by 0.46 m. Allowing for the motion of the helicopter, the 20-msec field of view was 14.02 m by 0.91 m with the long axis across the flight path. (See fig. 4.)

Data were acquired over time intervals of 1 min or more as the RSS field of view progressed from water outside the plume, across the plume, and to water outside the plume on the other side. The passes were made as close as possible to the sample station as indicated by the position of the ship illustrated in figure 4.

Chemical Analysis of the Sea-Truth Samples

Having prior knowledge of the typical composition of the acid waste solution (table I), the components most likely to have an influence on spectral signatures were selected beforehand for analysis, and the collection of sufficient volumes of samples was planned in the test program. Water samples were taken at depths of 0, 4, and 8 m with 5-liter Niskin bottles. These samples were then divided into five 1-liter samples for each depth at each sampling station. At some stations, a surface sample was taken by plastic bucket. This was a more accurate surface sample than the 0-m bottle sample which was actually drawn from a depth of about 0.46 m. A portable pH meter was used to measure the pH of each sample as soon as possible after the samples were brought onboard. Samples (500 ml) for chlorophyll analysis were refrigerated aboard ship and were filtered as soon as the ship got back to shore in the University of Delaware laboratories at Lewes, Delaware. The filters containing the phytoplankton (chlorophyll) were placed in opaque containers and refrigerated until analyzed. All other samples were refrigerated and transported in ice chests to the laboratories, where they were stored in refrigerators until analyzed. A schedule of the samples taken is given in reference 5.

The water samples were filtered through 0.45- μ m filters and were separately analyzed for the following metallic constituents in the filtrate (solution) and the residue (solids): iron, manganese, chromium, vanadium, titanium, aluminum, and zinc. Sulfate ion, salinity, total suspended inorganics (non-

volatile), and total suspended organics (volatile) were also determined for these samples.

The analyses for metals were conducted using atomic absorption methods; sulfate, by a turbidimetric method; salinity, by silver nitrate titration; suspended solids, by standard heating and weighing methods; and chlorophyll a, by the Strickland and Parsons method. (See ref. 6, pp. 185-192.) A sample of ocean water from outside the dump area and a sample of the acid waste from the barge were also obtained and analyzed by the same methods used for the plume water samples.

Laboratory Experiments

Studies were performed in the laboratory to determine what occurs chemically and spectrally as the acid waste is diluted with ocean water collected from the general vicinity of the dump area. Six successive tenfold dilutions were performed, and the pH was measured after each dilution step. The same series of dilutions of acid waste were made with distilled water and pH measurements were made for comparison with the ocean-water dilutions. The same series of dilution of acid waste with ocean water was used to obtain the spectral transmission curves for the various concentrations produced. The spectral transmission curves were obtained over the wavelength range of 300 to 1100 nm with the same RSS instrument which had been used for the on-site remote-sensing measurements. Visual observations including color changes and appearance or disappearance of precipitates in the dilution solutions were noted. Thus, changes in spectral (color) character with dilution were determined for use in relating remotely sensed data to concentration and spectral signatures.

In order to do these laboratory studies, the RSS was set up on an optical bench which included a tungsten-filament standard lamp for illumination and a sample compartment adjacent to the RSS sensing unit slit so that sample cells could be positioned in the light beam between the source and slit for spectral beam transmission measurements. Spectral transmission measurements were made for a path length of 5 cm and with and without a ground glass diffuser plate behind the sample cells.

A synthetic acid waste solution was made up of ferric chloride, hydrochloric acid, and sodium sulfate in distilled water to match the concentrations of iron, acid, and sulfate in the acid waste sample. The spectral transmission curves of the synthetic solution and its successive dilutions with ocean water were obtained. These curves were compared with those for the actual acid in order to see if the components chosen were in fact the components of the acid waste which were responsible for the shape of the spectral signatures observed.

DATA ANALYSIS, RESULTS, AND DISCUSSION

Remote Sensing With the RSS

The field data, recorded on analog tape, included three passes over the plume for each station. Each pass produced data for one of the RSS spectral

ranges: 300 to 700 nm, 500 to 900 nm, and 700 to 1100 nm. For each range, data were taken for instrument baseline, clear water (out of plume), plume water, and clear water, in that sequence. A range was scanned every 20 msec for the duration of the data-taking part of the pass (about 1 min); thus, the many scans produced an almost continuous record of any spectral radiance changes across the plume.

To reduce the data to usable form, the following procedure was used: Oscillograph records of the analog tapes were made for each range at each station. From these, typical spectral curves for the unpolluted water on either side of the plume were selected for digitizing, and all spectral scans in the plume were digitized and put on digital tape for computer data reduction and manipulation. The spectral scans were each divided into 100 4-nm-wide bands, and each was given a relative vertical deflection value which was proportional to the spectral radiance for each 4-nm band. Each of the vertical deflection values was corrected for the instrument baseline and lens transmission to give relative radiance values for each 4-nm band. From these relative radiance values, curves of spectral change with time (distance) as the field of view swept from clear water, into the plume, and out into clear water again were constructed by the computer.

Figures 6 and 7 show a series of a few selected curves of relative radiance over a given wavelength range which show the change of radiance with position across the acid waste plume. The highest peak radiance in the 400- to 700-nm range occurs in the most concentrated part of the plume, and the lowest radiance occurs at the edge or in water outside of the visible plume. It can be seen that only small changes in radiance with concentration occurred below 400 nm and beyond 700 nm. This indicates that the acid waste has negligible concentration-dependent spectral reflectance characteristics at those wavelengths. The shapes of these spectral curves between 400 and 700 nm are taken to be the spectral signature of this type of acid waste in ocean water. A possible method to determine the concentration of the acid waste would use the ratio of the radiance at two different wavelengths since this ratio changes significantly with concentration. However, this method would depend on the availability of suitable calibration techniques. As will be seen, the data obtained in this test were not adequate to provide calibration over a large enough concentration range for this purpose. One factor was that only two stations, 1-0 and 1-1A, gave good RSS data; the others were affected by sunglint and could not be used. This meant that only two sea-truth points were applicable and there is some question about the registration of the sea-truth data with the RSS remote-sensing data.

Chemical Analysis of the Sea-Truth Samples

The results of the 31 sea-truth water sample analyses are summarized in table II. The table gives designation of station, depth and age of plume, and analysis results for pH, salinity, suspended solids, iron, manganese, and zinc. The other metals analyzed had concentrations below the detection limits of the atomic absorption methods used (chromium <0.05 mg/liter, vanadium <8.0 mg/liter, titanium <10.0 mg/liter, and aluminum <2.0 mg/liter) and thus are not included in table II. Sulfate concentration for all samples (not given in table II) was

constant at 2600 mg/liter \pm 10 percent, a level typical of ocean water. Salinity was relatively constant in the range from 31.0 to 32.4 parts per thousand. Values of pH ranged from 7.7 to 8.1. Total organic (volatile) suspended solids ranged from 0.3 to 9.5 mg/liter, and the total inorganic (nonvolatile) suspended solids ranged from 0.8 to 5.6 mg/liter, with the surface samples generally having the higher concentrations for both. Chlorophyll a content ranged from 0.99 to 2.2 μ g/liter, with the average close to 1.5 μ g/liter.

Table II is arranged according to the age of the acid waste plume when the sample was taken and according to increasing sampling depth at each station. The plume age for the samples ranged from 1 hr, 37 min to 4 hr. The samples were taken between 8:50 a.m. and 1:30 p.m. EDT. The plume-age spread should have resulted in a range of pollutant concentrations in the plume corresponding to different amounts of dilution by dispersion, but the analyses of the samples did not show any particular trend with plume age. Neither the pH nor the iron concentration showed a consistent decrease with age of the plume for the samples taken. Other evidence such as aerial photographs and remote-sensing data obtained during this test (ref. 5) indicates that the plume did not disperse quickly but kept fairly sharp, though jagged, boundaries over the duration of the dump (5 to 6 hr). From what has been observed in laboratory studies, it is believed that the major part of the dilution of the acid should take place within about 30 min after leaving the barge and then only slowly thereafter. The data obtained on this particular day support these observations; however, a more severe sea state could change the picture.

Table II indicates that there are trends with depth at a given station. The suspended material (solids) was generally higher in concentration at the surface, was lower at 4-m depth and, in the three cases where there were data at 8 m, increased again at the 8-m depth. One of these cases was for the station outside the plume, so it appears that the stratified distribution was normal in the area at that time. During the dump and sampling time, the depths of the thermocline changed from about 12 m at 9:05 a.m. EDT to 5 m at 1:40 p.m. EDT, which probably had an influence on the vertical distribution of suspended material. Stations 1 through 3 were sampled between 8:45 and 11:15 a.m. EDT, and stations 4-1 to 4-5 were sampled between 12:30 and 1:30 p.m. EDT (ref. 5). It is perhaps significant that the out-of-plume station (1-2) had higher concentrations of suspended solids at the 8-m depth than at the surface, the reverse of the plume stations. This may be due to a different particle size distribution.

In plotting the concentration data of table II for the metals and suspended solids against plume age, it became evident that some extraneous factor was influencing the data since there was little correlation with age at a given depth. Also, one station (1-1A) of intermediate age appeared to be quite out of line compared with most of the other plume stations. Since these kinds of results could be a result of sampling irregularities, the sampling procedures were reviewed and the photographs taken from the helicopter during the samplings were studied. It was discovered that although the ship was nominally in the middle of the plume when taking samples, sometimes it was not. For station 1-1A, which had apparently anomalous results, it was found that the samples were taken at a station which was in or near a clearer channel of ocean water running transversely through the plume and into which only a little of

the plume had dispersed. Another factor found to contribute to the poor correlation was the fact that the Niskin bottles were not shaken before the removal of the 1-liter samples to insure homogeneous distribution of suspended solids for each of the five samples withdrawn. Neither was the order of 1-liter samples withdrawn for the various analyses the same in each case so that the first portions probably had more suspended solids or different types than the last ones as a result of settling. In spite of these shortcomings in the data, some definite trends with depth were found which were largely independent of these sampling problems.

The iron in the acid waste solution was present initially at a concentration of 20 600 mg/liter. The analysis for iron in solution for the plume samples was found to be in error due to sulfate interference in the atomic absorption analysis. Experience with this type of interference indicated that the iron concentration of the samples was below the normal detection limit of the method, and thus, the concentrations given in table II are less than 0.05 mg/liter for all ocean water samples.

The iron in the suspended material (filtered out and analyzed separately) did not have sulfate interference and gave good results. The data of table II show a fairly consistent decrease in the concentration of suspended particulate iron with depth, the surface (bucket) samples having the highest concentrations. Where this trend is not shown, it is thought that the sample had been taken at a part of the plume where clearer ocean water may have been intruding into the plume locally, giving a different distribution. In the case of station 1-1A, this is known to be true. Visual observations and photographs from aircraft had revealed obvious variations in plume dispersion characteristics locally all along the plume. Therefore, it is not surprising that the same trends or patterns did not show up in all the samples. Further evidence that the trend of decreasing concentration with depth is real is given by the results of the manganese and zinc in solution, where the same trend prevails for most of the samples. (See table II.)

Another sea-truth measurement which may have some use in interpreting the remotely sensed data is Secchi depth, which varied from 2.25 m to 3.5 m and averaged 3 m for the stations in the plume. The station out of the plume (1-2) had a Secchi depth of 4.25 m. These readings indicate an ocean condition quite a bit more turbid than usually expected that far offshore.

Laboratory Experiments

Experiments were performed in the laboratory to supplement the sea-truth data and to gain an understanding of the chemical interaction of the acid waste and ocean water and resultant spectral changes.

Tenfold dilutions of the acid waste with ocean water were successively performed and the pH was measured within a few minutes of each dilution. Figure 8 shows the data in graphical form for two different acid waste samples (AW-1 and AW-2) diluted with ocean water (SW-1), an acid waste diluted with distilled water, and one normal hydrochloric acid solution (1N HCl) diluted with distilled water (DW). These curves show that both acid and acid waste,

when diluted with distilled water, gave essentially the same linear change in pH from the undiluted state to the 1:10⁵ dilution, with the curves leveling off at the pH of distilled water (about pH = 5). In contrast, the curve for acid waste diluted with ocean water was not linear, there being a relatively large positive change in slope at the 1:10² dilution and a leveling-off stage at about the 1:10⁴ dilution at a pH of 8, which is the pH of the ocean water alone. This nonlinearity is a result of diluting the acid waste with a slightly alkaline buffered solution (ocean water, pH 8).

The visual appearance of the dilution solutions is given in table III. The color changes and the appearance of a gelatinous precipitate in the 1:10³ dilution solution are characteristic of the acid waste from this particular source. It should be noted that the precipitation in the 1:10³ dilution solution coincides with the marked increase in slope of the pH curve for acid waste diluted with ocean water. Further, it is observed that when the 1:10³ dilution solution containing the suspended precipitate is allowed to stand without shaking, the precipitate agglomerates and falls to the bottom of the vessel and forms an orange-brown coating on the bottom, which can easily be redispersed with shaking. When the precipitate is on the bottom, the solution is clear and colorless, an indication that the yellow ferric ion has precipitated out.

The precipitate is some form of ferric hydroxide, Fe(OH)₃, the expected product when the pH is increased by dilution or by addition of an alkaline solution. In this case, precipitation occurred when the pH of the acid waste solution exceeded 2.87, that is, when the 1:10² dilution solution (pH = 2.75) was further diluted to 1:10³. The pH = 2.87 precipitation point was obtained by calculation using the solubility product constant K_{sp} for Fe(OH)₃ of 1.5 × 10⁻³⁶ and the known concentration of iron in the acid waste (20.6 gm/liter), which would give its concentration in the 1:10² dilution solution. The pH and hydrogen ion concentration [H⁺] in moles/liter were calculated using the following equations:

$$K_{sp} = [Fe^{+3}] [OH^{-}]^3 = \frac{[Fe^{+3}]}{[H^{+}]^3} \times 10^{-42}$$

where

$$[OH^{-}]^3 = \frac{(10^{-14})^3}{[H^{+}]^3}$$

$$K_{sp} = 1.5 \times 10^{-36}$$

$$pH = \log \frac{1}{[H^{+}]}$$

Spectral transmission curves of the diluted acid waste solutions obtained under various conditions are shown in figures 9, 10, and 11. Figures 9 and 11 are beam transmission measurements, whereas figure 10 is measured with a ground glass diffuser behind the sample cells and is termed a diffused transmission. The curves of figures 9 and 11 were made from laboratory measurements of acid waste and synthetic acid waste solutions, respectively, using the RSS instrument setup on an optical bench with a sample cell having a 5-cm path length. The percent transmission, based on ocean water having 100-percent transmission, at each wavelength is plotted against the wavelength in nanometers at 20-nm intervals for the range of 400 to 1100 nm. The range where the significant color changes occur, however, is 400 to 700 nm. Figure 10 was obtained for acid waste solutions using the same 5-cm cells but with a prism spectrophotometer.

It can readily be seen from these curves that dilution produces a color change by the shifting of the absorption edge toward lower wavelengths as the solutions become more dilute. Color is also changed by the lesser effect of absorption as dilution increases. There is, however, one apparently anomalous curve, the one for the $1:10^3$ dilution, which has a more gradual decrease in absorption with a shift toward larger wavelengths compared with the preceding dilution solutions. This is the dilution where we had previously noted that a precipitate had formed and the color intensity had increased rather than diminished with the tenfold dilution step. This is also the dilution where pH increased much more rapidly than for dilution with distilled water. This spectral signature feature is quite repeatable and is related to the chemical characteristics of the acid waste/ocean water system as described in the discussion of pH changes. It should also be noted that the curves for the $1:10^4$ and $1:10^5$ dilutions follow the shape of the $1:10^3$ curve as they represent increased transmission due to dilution of particulate $\text{Fe}(\text{OH})_3$.

Figure 11 gives the curves for the synthetic acid waste solution for the various dilutions. The almost identical characteristics of this solution to the real acid waste solution support the belief that the Fe^{+3} ion is the source of the spectral signature of this type acid waste. This leads to the conclusion that iron, which is only one component of a multicomponent waste solution, is in fact, a spectral indicator for this type of acid waste.

Comparison of the curves of figures 9, 10, and 11 shows that the characteristic shapes of a given dilution solution curve are very similar for each of the various measurements. The relative transmission at any given wavelength may vary with the measurement conditions but the shapes remain similar, which means essentially that the spectral signature is established for this type of acid waste in ocean water.

Field and Laboratory Data Relationships

By combining the data, a rough method for estimating the acid waste concentration of ocean dump plumes was derived by Henri Hodara from Tetra Tech, Inc. and was obtained from him through personal communication. The method relies on a simple mathematical model which treats the pollutant plume as a layer through which the solar light passes twice (once down into the water and

once back up through the water) before being returned (reflected skyward) from the ocean surface. (Refer to appendix for further details of the method.) Laboratory measurements with the RSS or a laboratory spectrophotometer provide spectral transmissivity values (figs. 9, 10, and 11) for a range of concentrations of the pollutant (acid waste) diluted with ocean water from the same area. Spectral radiance of the ocean surface (surface reflected and upwelling light) is measured by the RSS across the ocean dump plume and includes the ocean water radiance outside of the plume (background). Spectral reflectance R_w' curves are constructed by multiplying the measured, out-of-the-plume spectral radiance of the background water R_w by the square of the spectral transmissivity τ' for each of several concentrations of pollutant in ocean water; that is, $R_w' = R_w(\tau')^2$.

The shapes of the R_w' spectral curves (normalized to the peak radiance of the remote data curve) are then compared with the remotely measured spectral reflectance curves (figs. 6 and 7) for the plume water. The R_w' curve for the concentration that most nearly matches the shape of the remotely sensed curve gives an adequate estimate of the pollutant concentration. Figure 12 illustrates this method for two different curves of data presented in figure 6. It shows that the R_w' dilution curve which most nearly reproduces the shape (color characteristics) of the remotely measured curve (solid line) used for this figure was the 1:10⁴ dilution curve in both cases, which represents an iron concentration of 2.06 mg/liter. The sea-truth concentration of particulate iron for this station (1-0) at the 0.46-m depth was 0.72 mg/liter (table II). Surface samples for similar age plume stations (2-2 and 2-3) averaged 2.1⁴ mg/liter. This agreement is excellent considering the assumptions and simplifications of the model used for this comparison.

Better curve matches and more accurate concentration estimates may be obtained by providing a number of transmission curves for solutions of intermediate concentrations between 1:10³ and 1:10⁵ dilutions. It may be fortuitous that the transmission curves obtained in the laboratory using a path length of 5 cm appear to approximate the effective depth-integrated attenuation effect measured by the RSS. However, considering other evidence, such as the particulate iron distribution of the plume surface water sample (highest at water surface) and the good agreement with particulate iron concentration of the sea-truth plume surface water samples, the model appears to be a reasonable approximation for this acid waste/ocean water system.

CONCLUDING REMARKS

It is concluded from this study that acid waste is a pollutant which can be monitored by remote-sensing techniques. Acid waste of the type studied - mostly ferric iron (Fe⁺³) dissolved in hydrochloric acid - has a recognizable ocean spectral reflectance signature which can be related to concentration through laboratory spectral transmission measurements of acid waste diluted to various concentrations with ocean water. This conclusion resulted from studies of the chemistry of the acid waste/ocean water system and the effects of their interactions on the spectral characteristics of the solutions and was supported by sea-truth data. These studies showed that iron, initially in solution as ferric chloride, was precipitated as Fe(OH)₃, a red-brown flocculent solid

having relatively large particle size. This precipitate remained close to the surface for a relatively long time. The highly radiant plume was visible quite readily down to particulate iron concentrations of 0.2 mg/liter, making it detectable over a wide concentration range. Even though the methods of quantification have not been fully developed because of the provisional nature of some of the sea-truth data and the relative rather than absolute radiance values obtained with the RSS, no serious problems are anticipated. For example, laboratory data for many intermediate concentrations may be readily obtained if needed.

The full spectral curves produced by the RSS and given in this report are applicable for identification purposes by other types of remote spectral sensors using bands in the 300- to 1100-nm range.

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May 18, 1977

APPENDIX

REMOTE-SENSING EQUATION AND APPLICATION

This appendix outlines the assumptions and simplifications made to develop the model used to calculate plume-reflected radiance from laboratory transmission data.

The basic spectral remote-sensing equation accounts for sky radiation incident upon the ocean surface being reflected off the surface and for radiation being transmitted into the water, refracted, and reflected or back-scattered up to and through the surface. Thus, there are three components of spectral radiance to be specified in order to determine what a remote sensor measures: (1) radiation scattered into the path by the atmosphere, (2) radiation reflected from the water surface, and (3) radiation upwelling from the water surface. The equation derived for the radiance N_{θ_a} arriving at a remote sensor looking at the surface at an angle θ_a from the zenith down at the ocean surface, with a sun angle of 30° or greater from the zenith (which avoids sunglint) and an optically infinite ocean depth (no bottom reflection), is given as

$$N_{\theta_a} = N_{\theta_a}^* + T_{\theta_a} \left[\rho(\theta_a) N_{sk}(\theta_a) + \frac{N_u(\theta_w) \tau_u(\theta_w)}{n^2} \right] \quad (1)$$

where all are spectral terms and where the first term in the brackets is $N_a(\theta_a)$, the radiance reflected off the water surface in air, and the second term is $N_w(\theta_a)$, the upwelling radiance from the surface in air. This last term contains the water-pollutant spectral signature information. In equation (1) $N_{\theta_a}^*$ is the path radiance between water surface and sensor, T_{θ_a} is the atmospheric transmittance, ρ is the reflectivity of the surface in air, $N_{sk}(\theta_a)$ is the sky radiance incident on the surface of the water, $N_u(\theta_w)$ is the upwelling radiance in the water just below the surface, $\tau_u(\theta_w)$ is the transmissivity of the water for upwelling radiation, and n is the refractive index of the water.

For application to a remote-sensing measurement where the sensor is looking at the nadir surface scene ($\theta_a = 0$) from an altitude of 609.6 m (2000 ft) or less ($N_{\theta_a=0}^*$ is negligible and $T_{\theta_a=0}$ is approximately 1), the equation can be reduced to

$$N_{\theta_a=0} = N_a(0) + N_w(0) \quad (2)$$

APPENDIX

Further simplification is made by assuming that $N_a(0)$ is negligible compared with $N_w(0)$ for the wavelength region of interest (i.e., visible below 600 nm), resulting in

$$N_a = N_w = \frac{\tau_u N_u}{n^2} \quad (3)$$

In water, the reflection coefficient R is the ratio of upwelling radiance to downwelling radiance N_u/N_d ; thus,

$$N_u = RN_d \quad (4)$$

and N_d in water is related to N_{sk} , the downward sky radiance by

$$N_d = \tau_d N_{sk} n^2 \quad (5)$$

where τ_d is the downward transmissivity through the water surface.

Substituting equations (4) and (5) into equation (3) gives

$$N_a = N_w = R\tau_u\tau_d N_{sk} \quad (6)$$

which is an equation for upwelling radiance from the ocean surface in the absence of a pollutant.

When a pollutant solution having a spectral transmissivity of τ' is dumped, τ_d and τ_u in equation (6) are modified to $\tau'\tau_d$ and $\tau'\tau_u$ and the radiance from the surface with pollutant N'_a is given by

$$N'_a = R\tau'\tau_u\tau'\tau_d N_{sk} \quad (7)$$

The ratio of radiance from the polluted and unpolluted ocean surface is simply

$$\frac{N'_a}{N_a} = \tau'^2 \quad (8)$$

APPENDIX

which allows calculation of the radiance expected from dump plumes of given concentrations if the transmissivity of the pollutant solution in ocean water for that concentration has been measured in the laboratory.

As used in the text, equation (8) was written as

$$R_{w'} = R_w(\tau')^2$$

where R_w is the measured relative reflected radiance of the out-of-plume ocean surface, $R_{w'}$ is the calculated plume relative radiance, and τ' is the laboratory measurement of transmissivity for a solution of pollutant in ocean water.

The model includes assumptions which require the pollutant to be essentially at the surface of an infinitely deep ocean, and in the present application, the effective "surface" thickness is of the order of 5 cm, the path length for which the transmissivity of the pollutant solutions τ' was measured in the laboratory.

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TABLE I.- TYPICAL ANALYSIS OF ACID WASTES FROM
TITANIUM DIOXIDE PROCESSING PLANT

[pH, 0.66; specific conductivity, 0.36 siemens/cm
at 20° C; specific gravity, 1.18997]

Waste constituents	Concentration, mg/kg
Total suspended solids	182
Total dissolved solids	228 949
Total solids	229 131
Oil and grease	49.0
Cl	14 210
NO ₃	13.2
P (total)	0.56
F	<1.0
CN	2.0
Sulfide	<0.05
SO ₄	58 819
As	<0.003
NH ₃	6.1
Kjeldahl nitrogen	8.9
Organic nitrogen	2.9
Phenols	0.04
BOD ^a	146
COD ^b	6393
TOC ^c	424
Ag	<0.2
Al	731
B	4.2
Ba	<0.5
Be	<0.2
Ca	26.9
Cd	0.4
Co	8.6
Cr	63.9
Cu	5.71
Fe	38 962
Hg	0.0062
K	16.8
Mg	180
Mn	1109
Mo	2.5
Na	101
Ni	8.6
Pb	10.1
Sb	8
Se	0.292
Sn	34
Ti	1580
V	153
Zn	35.3

^aBOD, biochemical oxygen demand.

^bCOD, chemical oxygen demand.

^cTOC, total organic carbon.

TABLE II.- CHEMICAL ANALYSIS OF SEA-TRUTH WATER SAMPLES

Age of plume, hr:min	Station	Depth, m	Suspended solids					Iron		Manganese		Zinc	
			pH (on site)	pH (lab)	Total organic (volatile), mg/liter	Total inorganic (nonvolatile), mg/liter	Total, mg/liter (a)	Salinity, ‰	In solution, mg/liter	In suspended solids, mg/liter (b)	In solution, mg/liter	In suspended solids, mg/liter	In solution, mg/liter
1:37	2-1	0	7.6	8.0	2.7	2.1	4.8	32.2	<.05	0.93	0.06	<.05	0.04
		4	6.9	8.0	1.2	1.6	2.8	32.2	<.05	.55	.05	<.05	.04
		8	7.6	8.1	---	---	---	32.2	<.05	.51	.05	<.05	.04
1:46	1-0	0	7.5	8.0	3.9	3.2	7.1	32.2	<.05	.72	.05	<.05	.05
		4	7.6	8.1	.5	.9	1.4	32.3	<.05	.22	<.05	<.05	.06
		8	7.7	8.1	---	---	---	32.1	<.05	.14	<.05	<.05	.05
1:46	2-2	^c 0	7.4	7.8	9.5	5.6	15.1	32.2	<.05	1.96	.08	<.05	.05
1:46	3-1	0	^d 6.7	8.0	3.3	2.3	5.6	31.8	<.05	.78	.05	<.05	.05
		4	7.5	8.0	2.7	2.0	4.7	32.0	<.05	1.06	.05	<.05	.04
		8	7.5	8.0	3.3	2.3	5.6	32.2	<.05	.88	.05	<.05	.04
1:50	2-3	^c 0	7.4	7.7	9.1	5.2	14.3	32.1	<.05	2.32	.09	<.05	.06
2:23	1-1A	0	7.6	8.1	.3	1.1	1.4	32.1	<.05	.21	.05	<.05	.04
		4	7.6	8.1	.8	1.2	2.0	32.2	<.05	.30	<.05	<.05	.04
		8	7.6	8.1	---	---	---	32.3	<.05	.40	<.05	<.05	.05
2:52	1-1B	0	7.6	8.0	1.5	1.6	3.1	32.2	<.05	.62	.05	<.05	.05
		4	7.5	8.0	2.1	1.9	4.0	32.4	<.05	.67	<.05	<.05	.05
		8	7.6	8.1	---	---	---	32.1	<.05	.42	<.05	<.05	.04

^aValues may vary by ± 10 percent.

^bValues may vary by ± 0.02 mg/liter.

^cSurface sample taken with bucket.

^dQuestionable value.

TABLE II.- Concluded

Age of plume, hr:min	Station	Depth, m	pH (on site)	pH (lab)	Suspended solids			Salinity, ‰	Iron		Manganese		Zinc
					Total organic (volatile), mg/liter	Total inorganic (nonvolatile), mg/liter	Total, mg/liter (a)		In solution, mg/liter	In suspended solids, mg/liter (b)	In solution, mg/liter	In suspended solids, mg/liter	In solution, mg/liter
3:07	4-1	^c 0	7.4, 7.5	8.0	3.8	3.7	7.5	31.8	<.05	1.03	0.06	<.05	0.05
3:10	4-2	0	.7.6	8.0	1.3	1.9	3.2	31.7	<.05	.77	.05	<.05	.09
		4	^d 6.6	8.0	1.0	1.1	2.1	31.8	<.05	.64	.05	<.05	.03
		8	^d 6.8	8.1	---	---	---	31.0	<.05	.32	.05	<.05	.05
3:32	4-3	^c 0	6.8	8.0	4.2	3.7	7.9	31.9	<.05	1.08	.06	<.05	.06
3:34	4-4	0	7.4	8.0	4.0	3.4	7.4	31.6	<.05	1.08	.06	<.05	.05
		4	7.6	8.0	1.3	1.1	2.4	32.1	<.05	.32	<.05	<.05	.04
		8	7.6	8.0	---	---	---	31.8	<.05	.21	<.05	<.05	.04
4:00	4-5	0	7.6	8.0	3.2	2.0	5.2	31.6	<.05	.70	.06	<.05	.05
		4	7.6	8.0	1.9	1.9	3.8	31.6	<.05	.62	.05	<.05	.04
		8	---	8.0	2.2	2.6	4.8	31.9	<.05	.51	<.05	<.05	.04
Out of plume	1-2	0	7.7	8.1	1.6	2.1	3.7	32.2	<.05	<.05	<.05	<.05	.04
		4	7.7	8.1	.3	.8	1.1	32.2	<.05	<.05	<.05	<.05	.04
		8	7.7	8.1	4.4	3.7	8.1	32.2	<.05	<.05	<.05	<.05	.04
Acid waste barge sample, undiluted			---	.6	---	---	---	----	20 600	----	780	----	50

^aValues may vary by ±10 percent.

^bValues may vary by ±0.02 mg/liter.

^cSurface sample taken with bucket.

^dQuestionable value.

TABLE III.- VISUAL CHANGES IN ACID WASTE SOLUTIONS ON DILUTION
WITH OCEAN WATER

Acid waste/ocean water solution	Color	Turbidity
Undiluted acid waste	Greenish yellow	Very slight
1:10	Light yellow	Clear
1:10 ²	Very light yellow	Clear
1:10 ³	Tannish yellow	Slight ^a
1:10 ⁴	Colorless	Clear
1:10 ⁵	Colorless	Clear

^aYellow-brown gelatinous precipitate present.

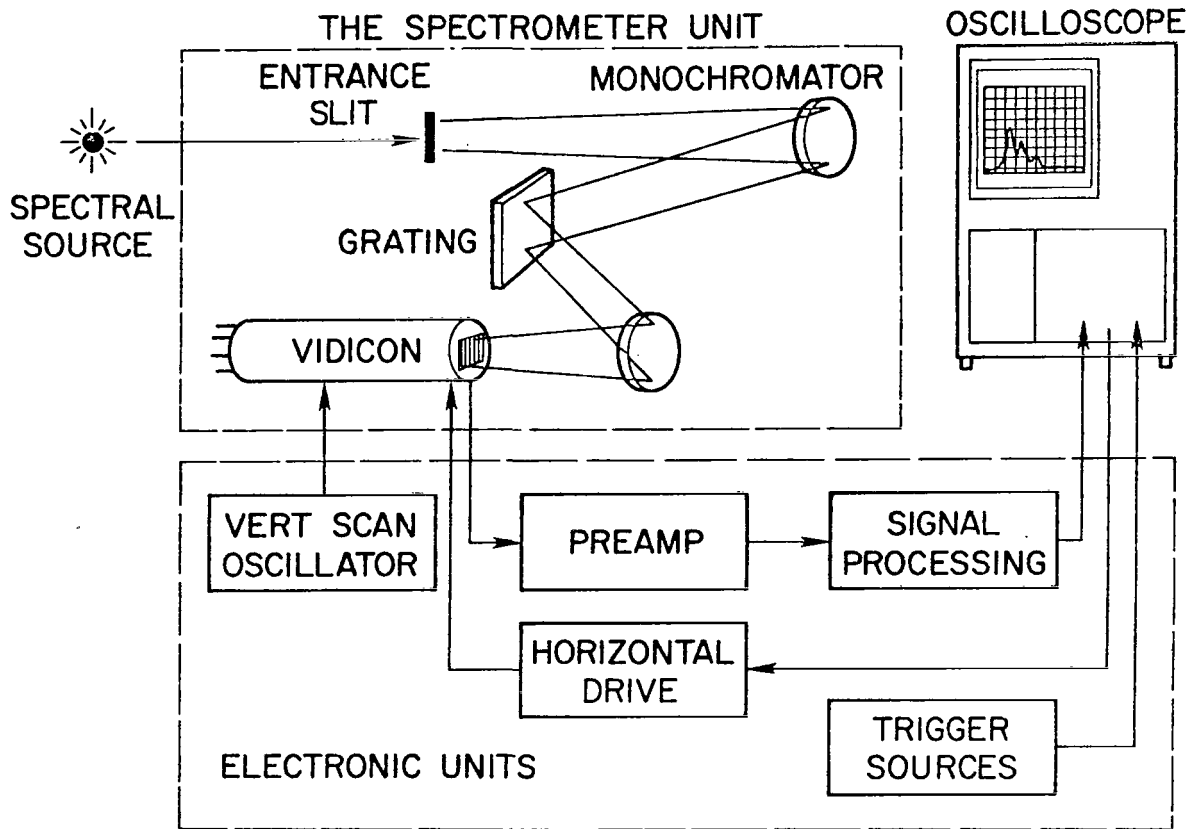
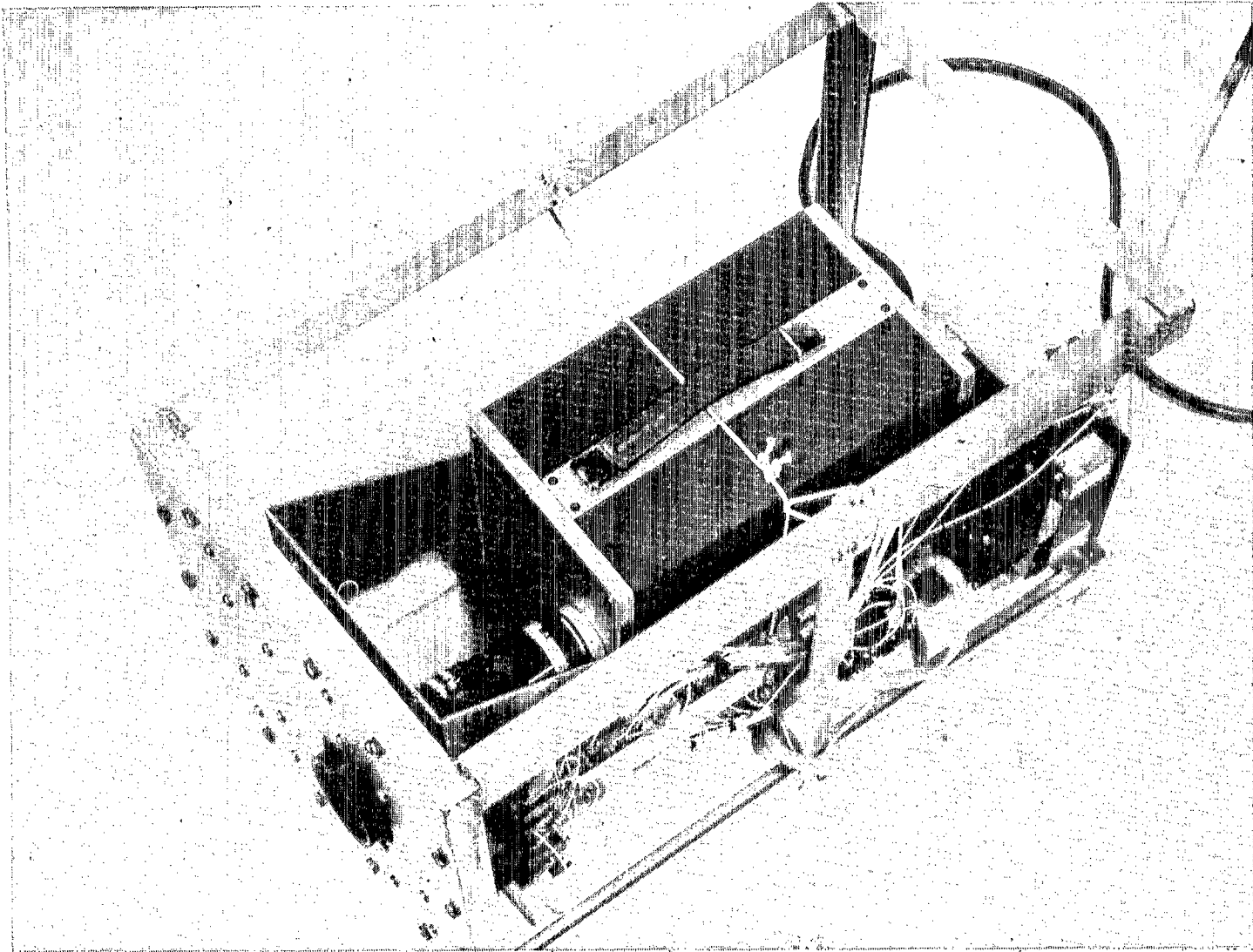


Figure 1.- Schematic of rapid scanning spectrometer.



L-75-6889

Figure 2.- Shock-mounted RSS module and lens.

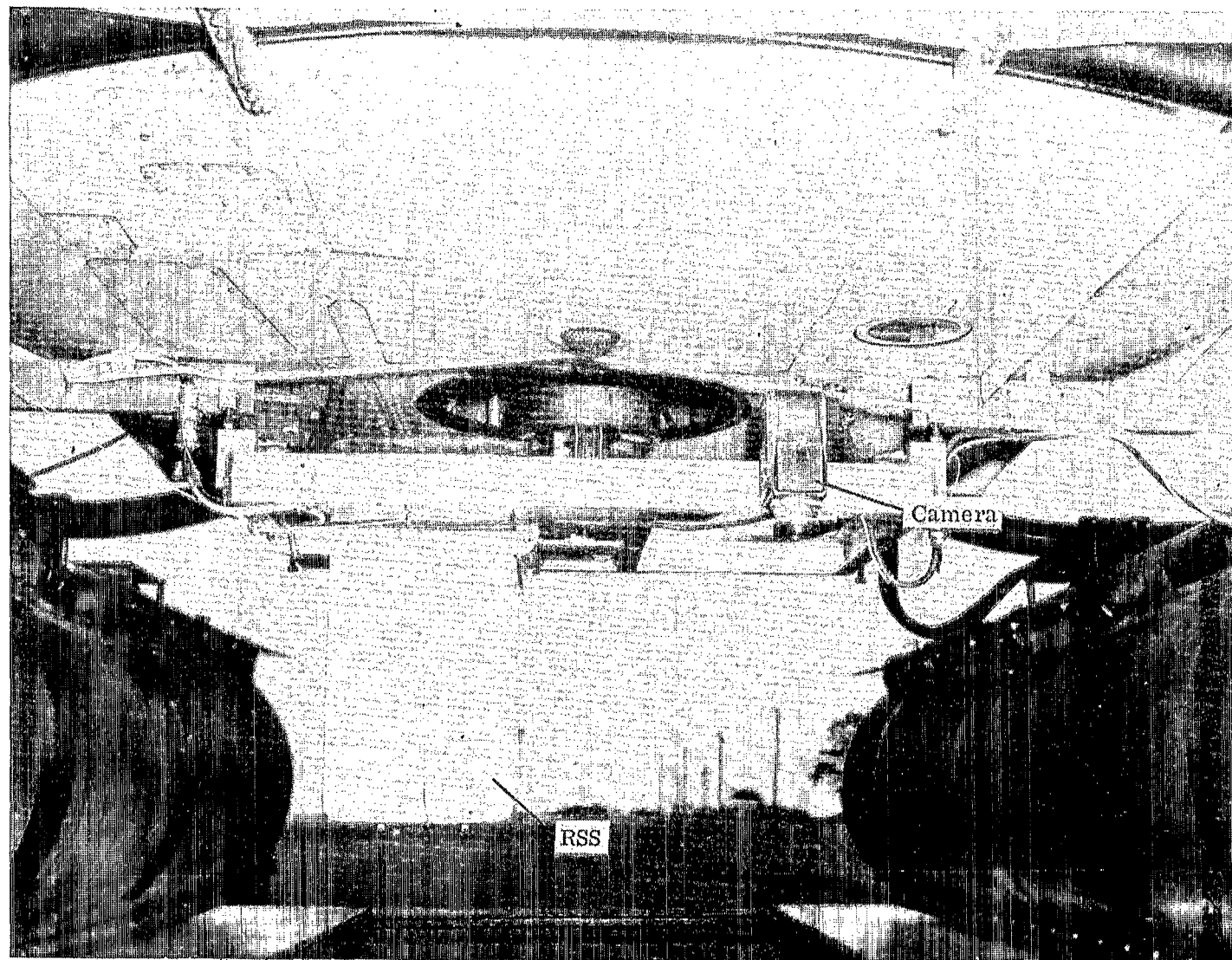


Figure 3.- Photograph of RSS and 70-mm camera mounted under helicopter. L-75-63.1

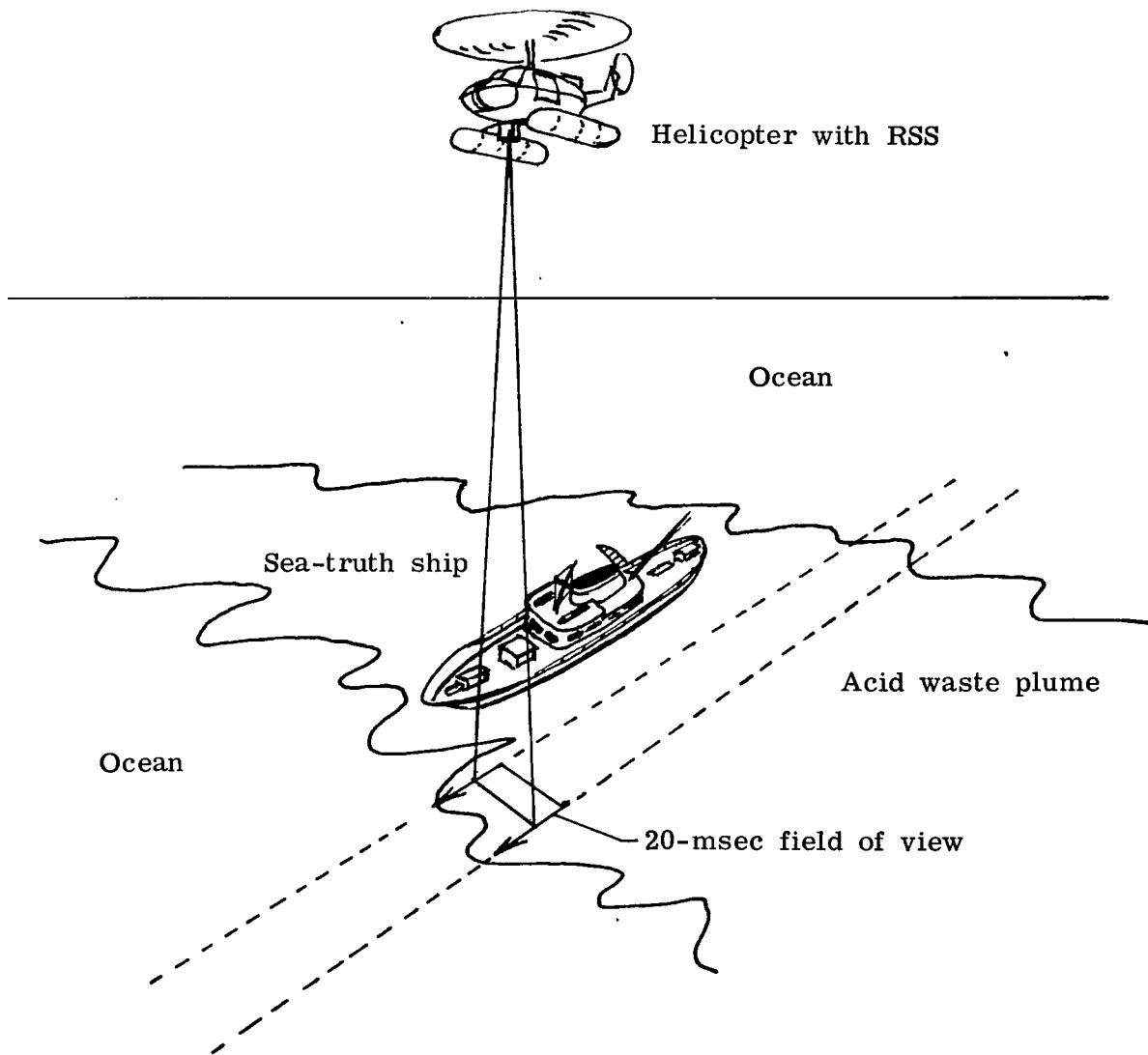
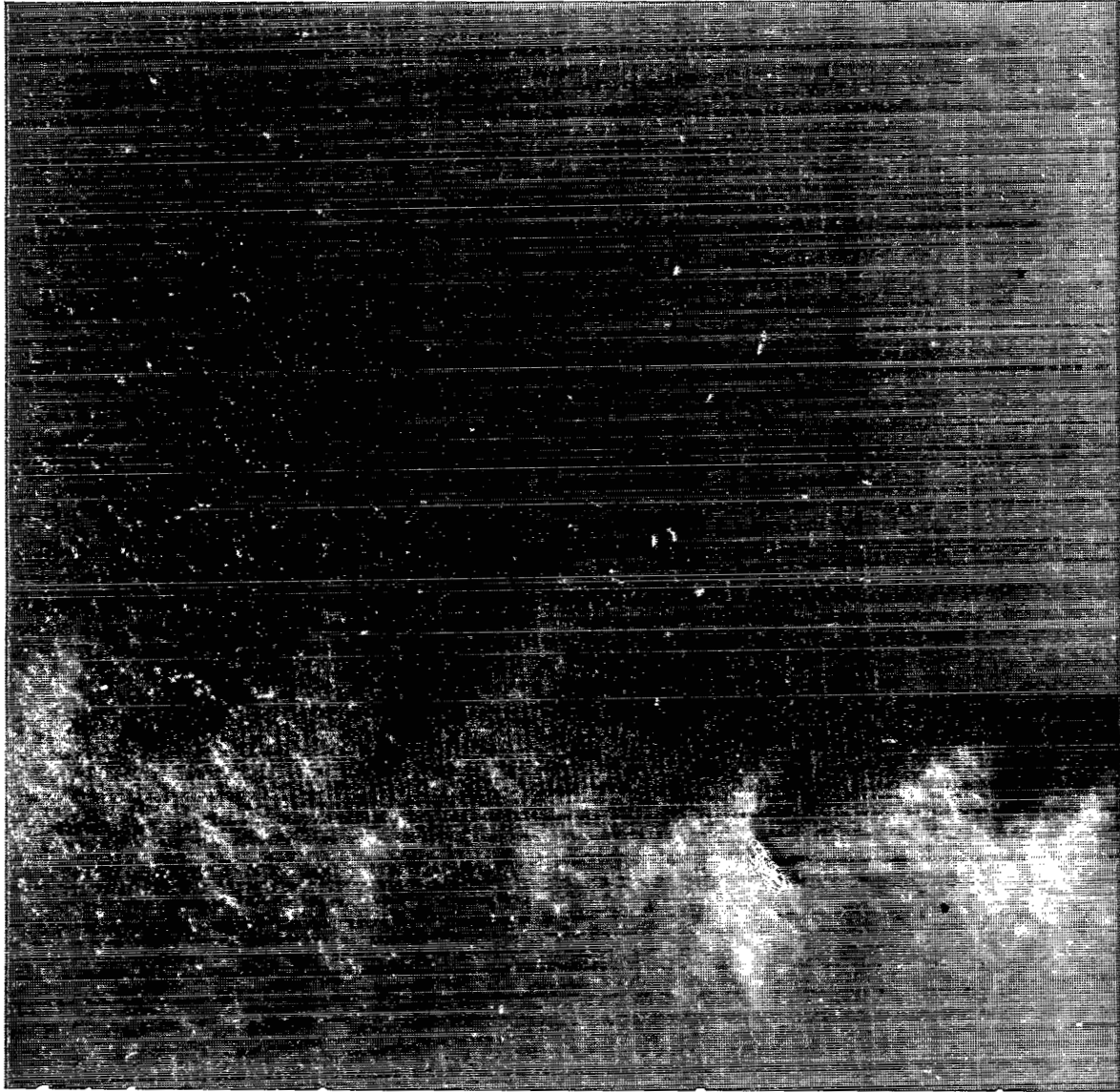
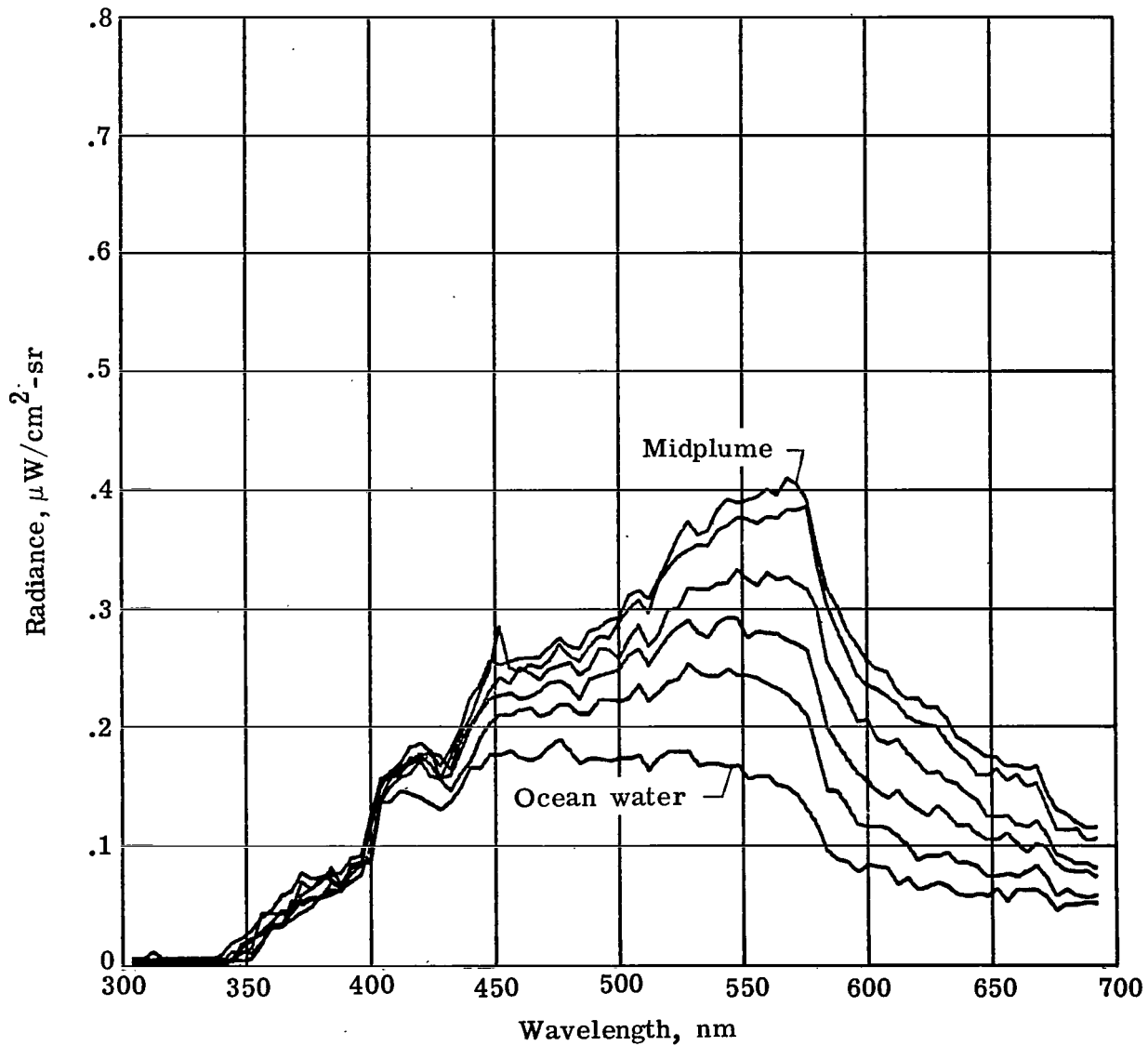


Figure 4.- Typical flight path of helicopter across plume, illustrating remote-sensing method used.



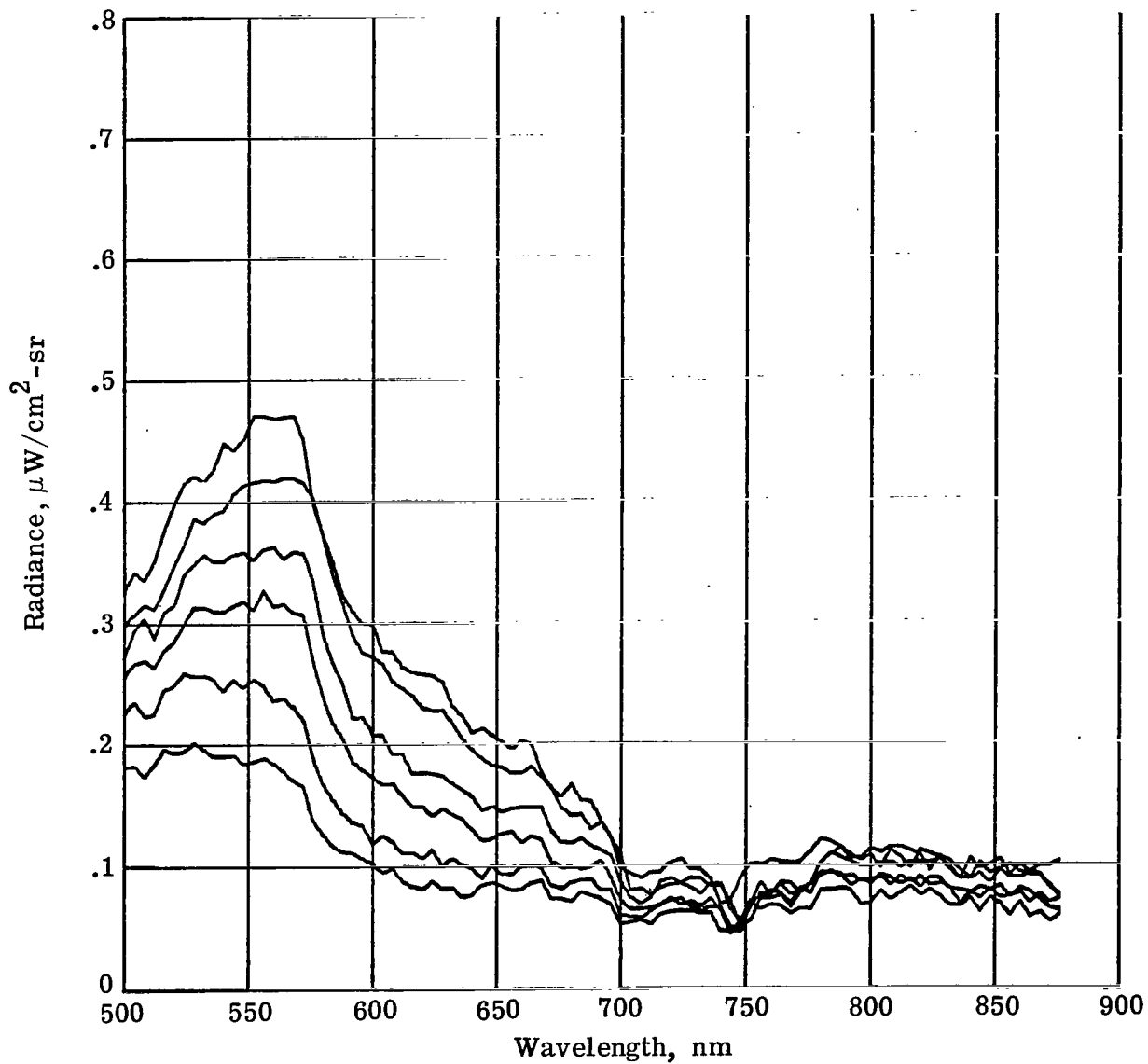
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Figure 5.- Photograph of RV Annandale in plume taken from
helicopter at altitude of 609.6 m (2000 ft).



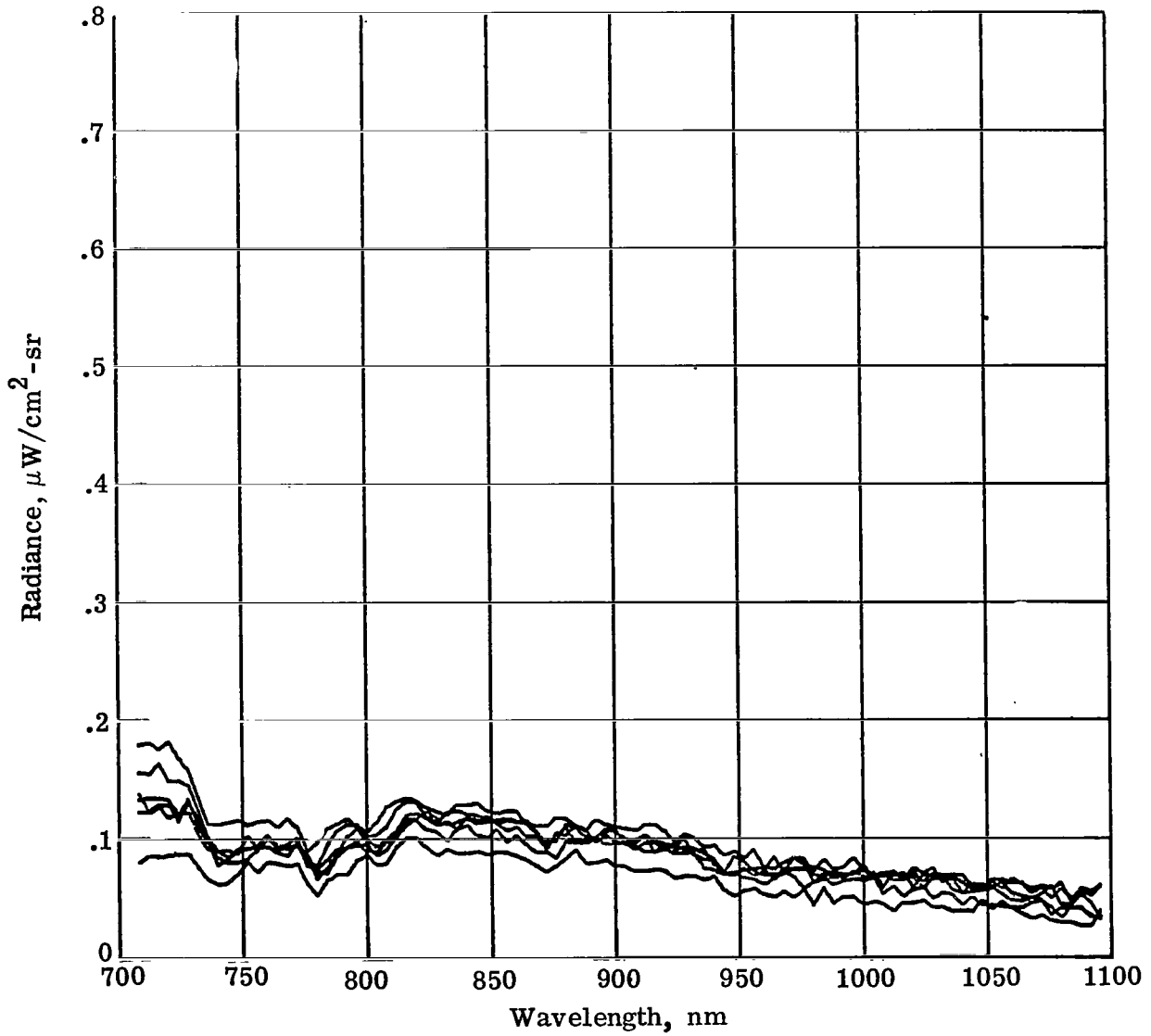
(a) 300- to 700-nm range.

Figure 6.- Spectral radiance changes across plume at station 1-0.



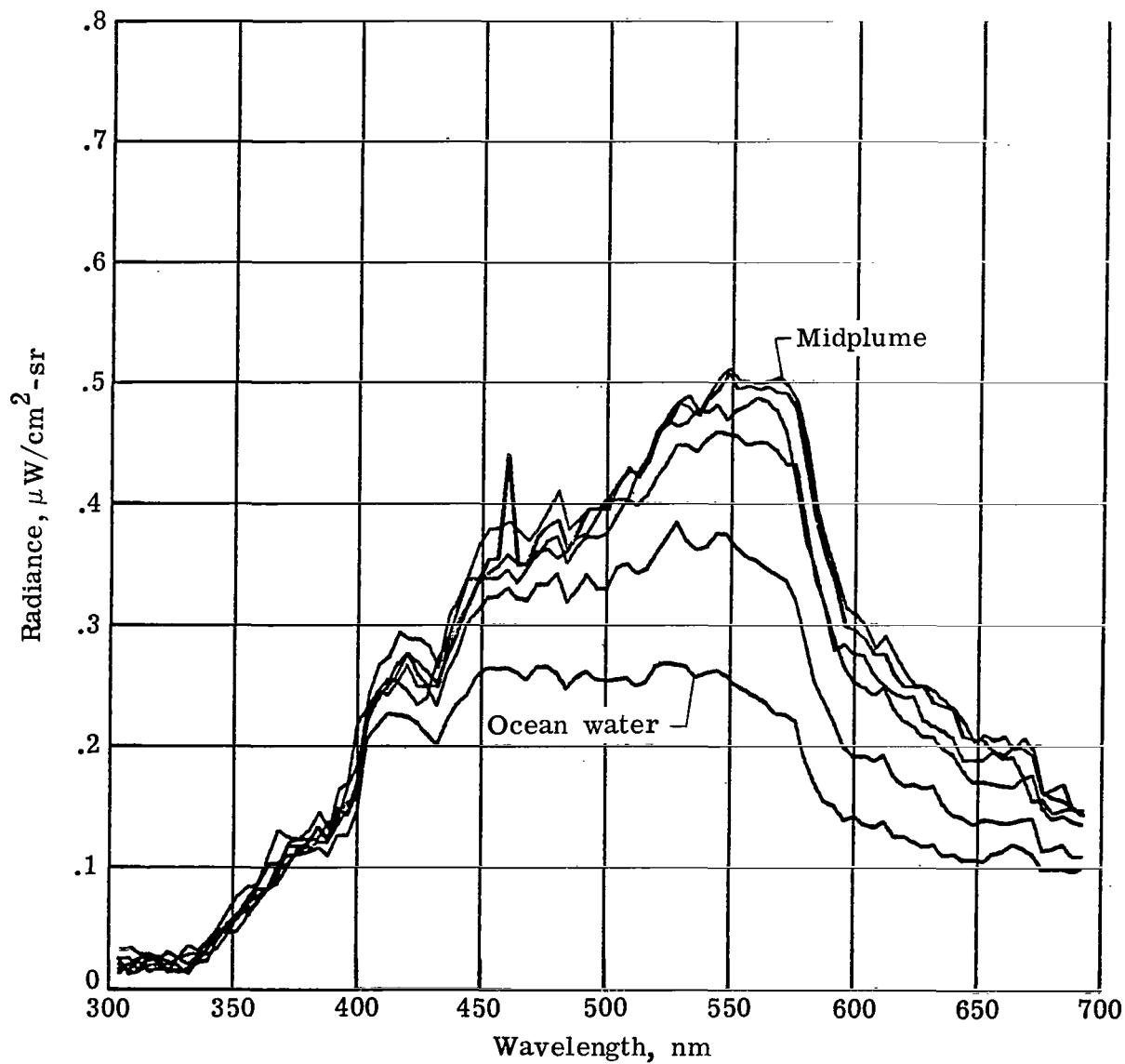
(b) 500- to 900-nm range.

Figure 6.- Continued.



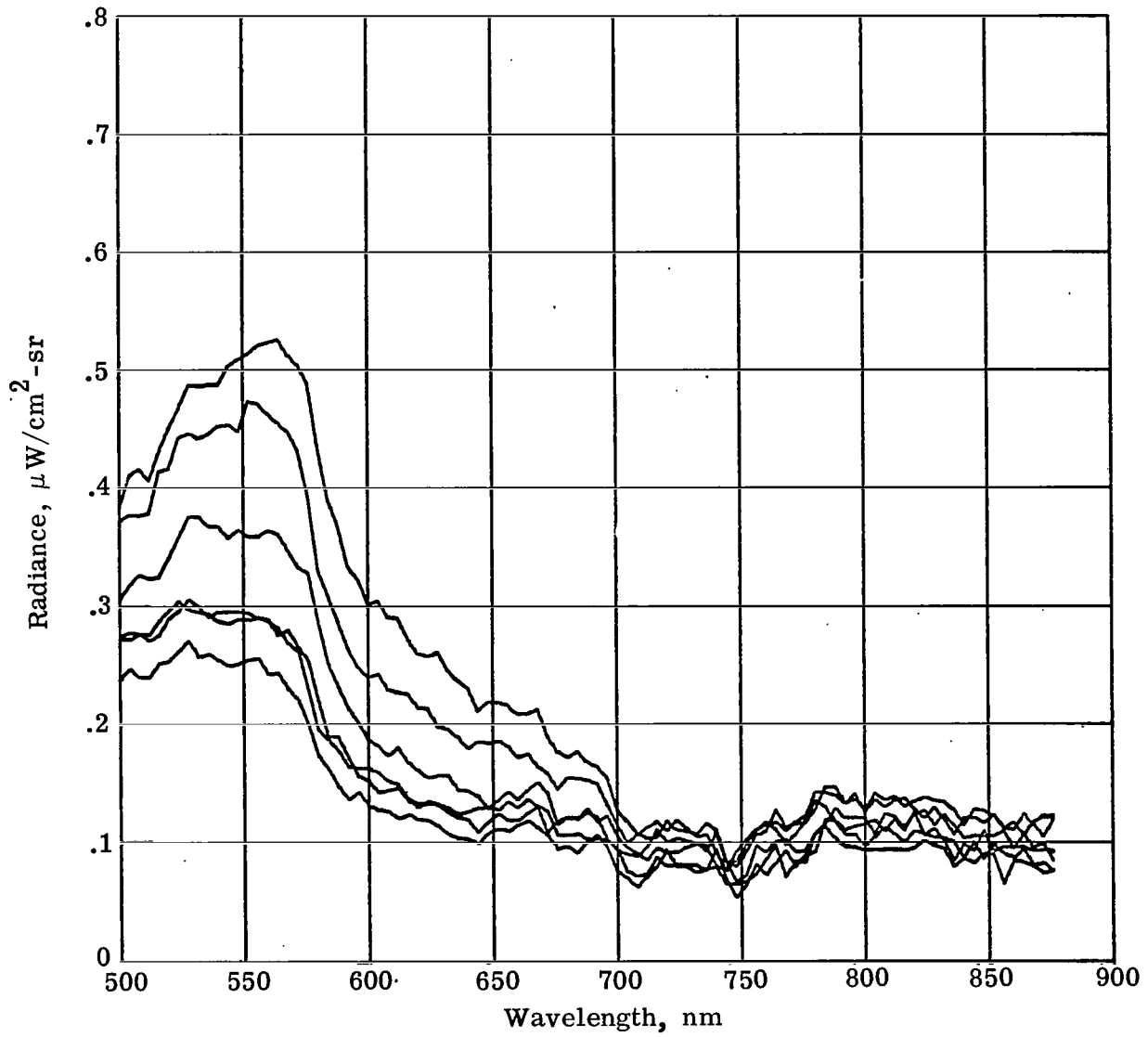
(c) 700- to 1100-nm range.

Figure 6.- Concluded.



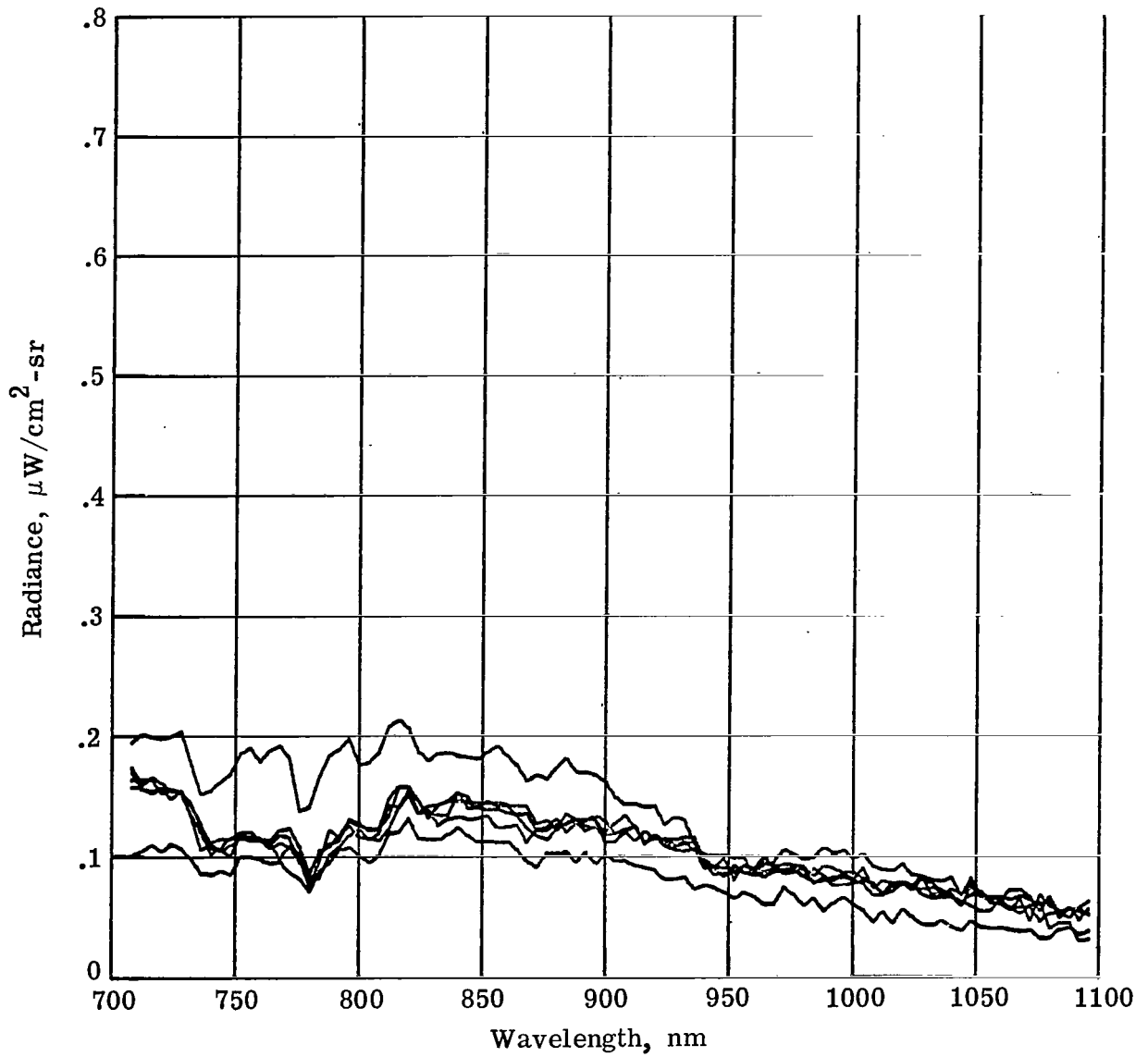
(a) 300- to 700-nm range.

Figure 7.- Spectral radiance changes across plume at station 1-1A.



(b) 500- to 900-nm range.

Figure 7.- Continued.



(c) 700- to 1100-nm range.

Figure 7.- Concluded.

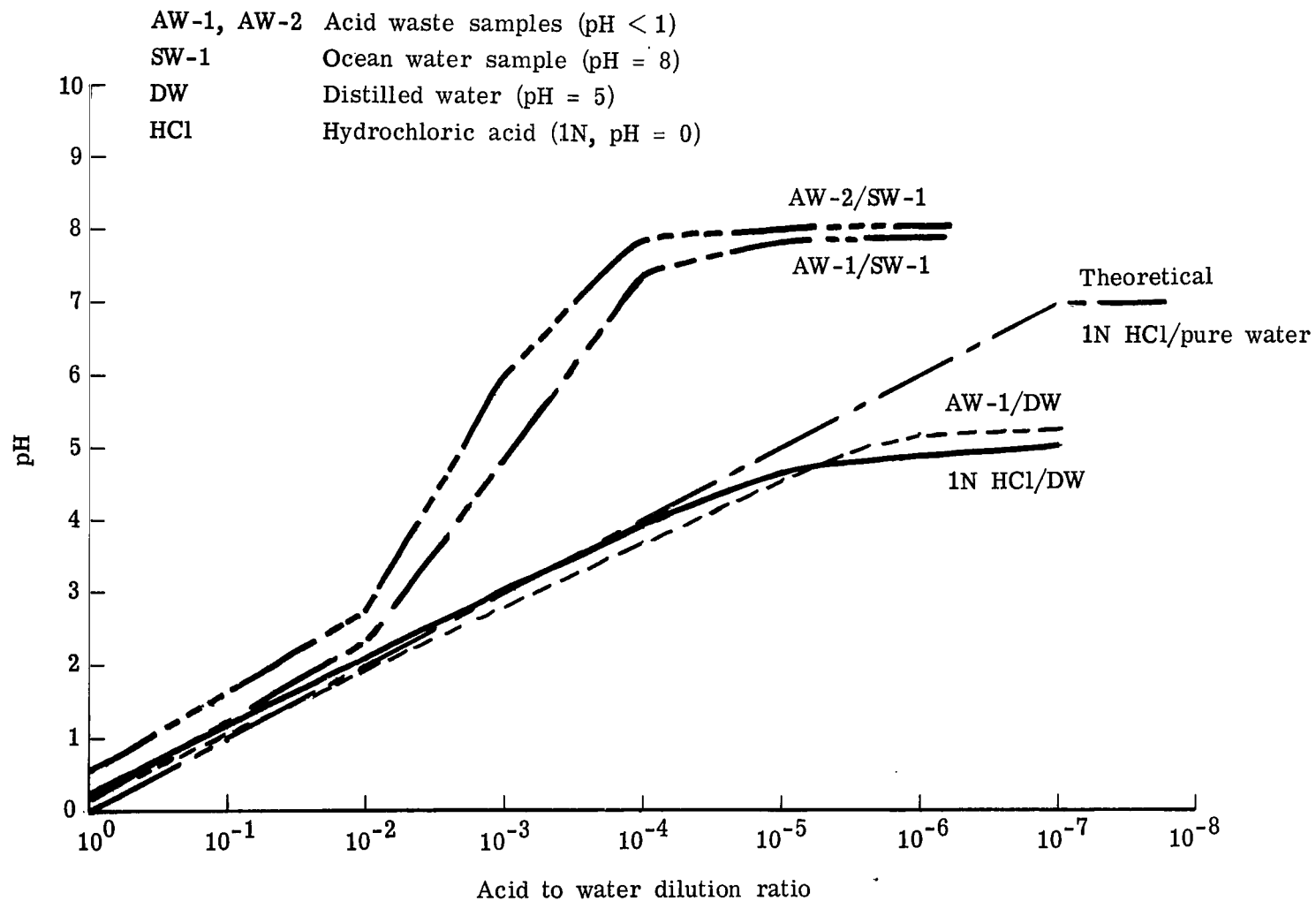


Figure 8.- Changes in pH of acid and acid waste solutions when diluted with ocean water or distilled water.

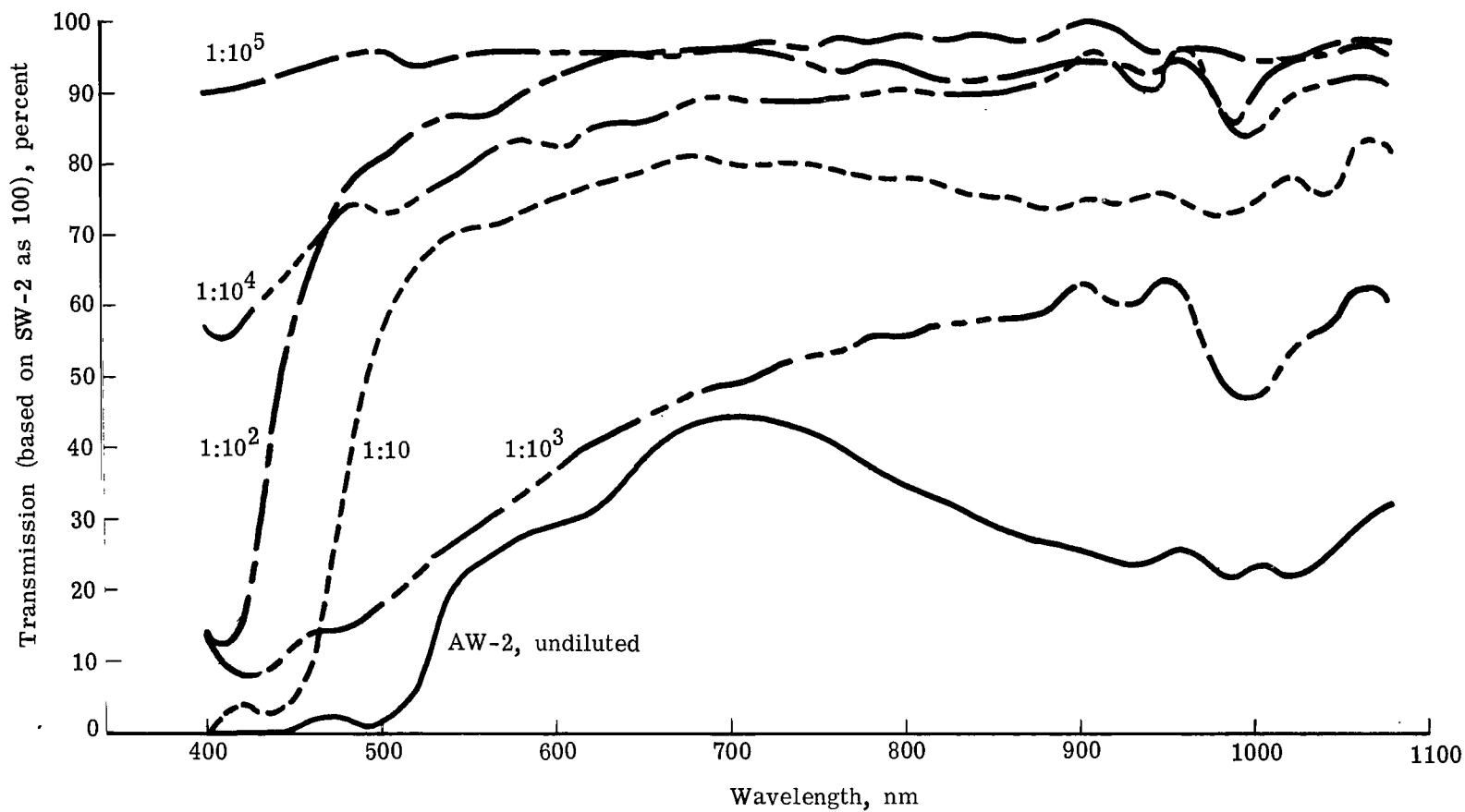


Figure 9.- Spectral transmission curves for acid waste solution (AW-2) diluted with ocean water (SW-2) from RSS measurements using 5-cm cells. Indicated ratios are for volumetric dilutions of AW-2 with SW-2.

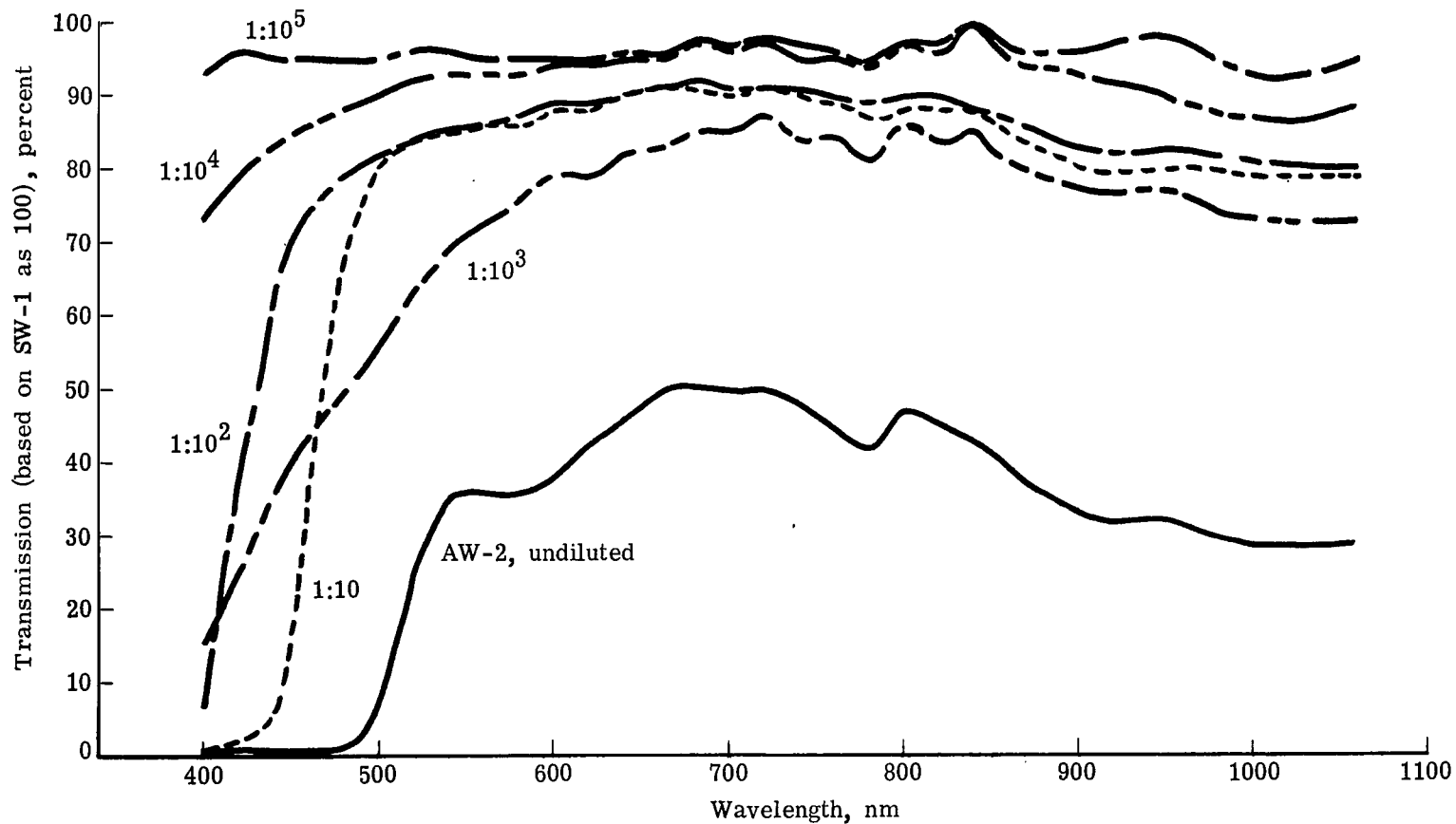


Figure 10.- Spectral transmission curves for acid waste solution (AW-2) diluted with ocean water (SW-1) from prism spectrophotometer measurements using 5-cm cells. Indicated ratios are for volumetric dilutions of AW-2 with SW-1.

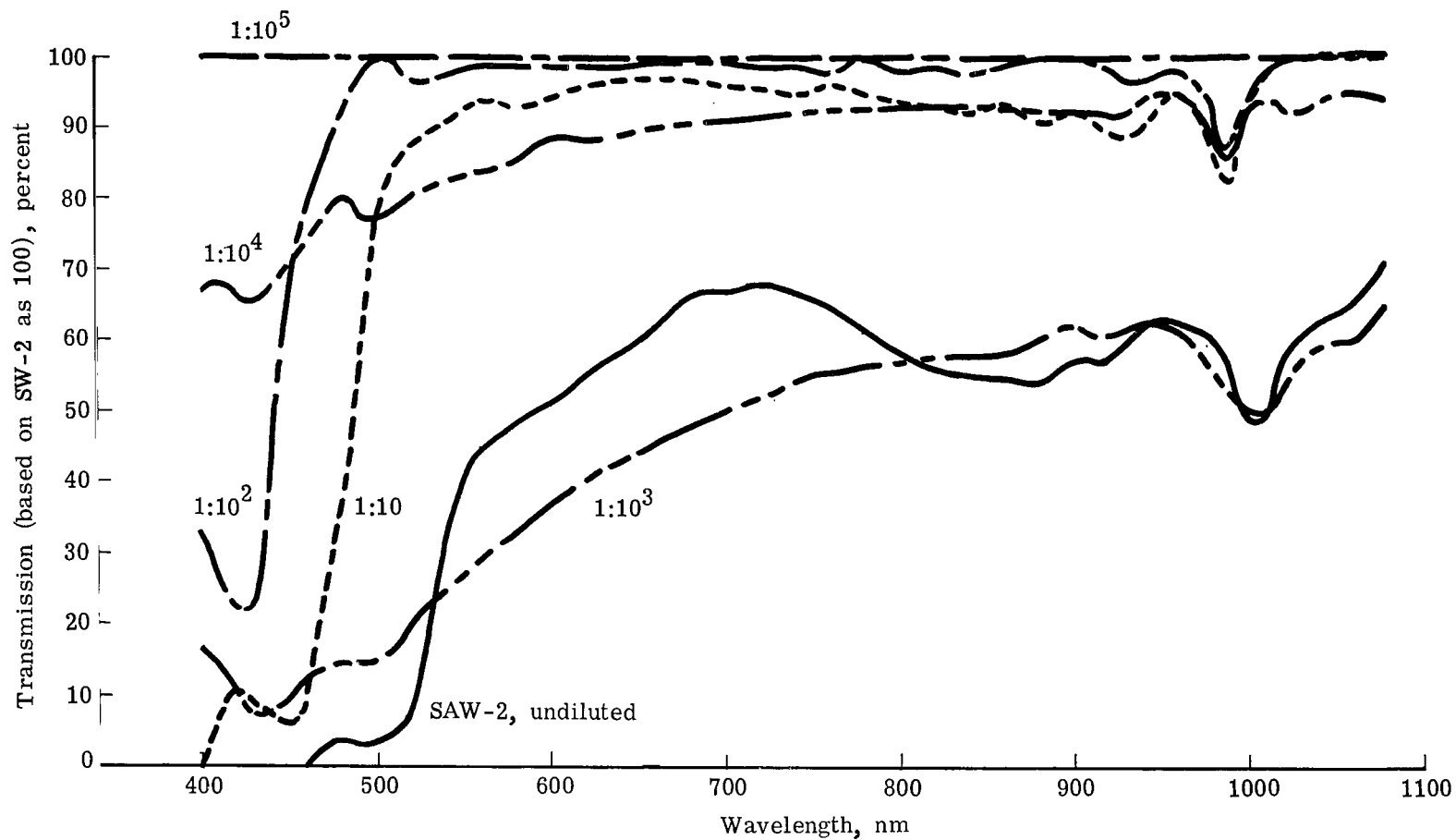
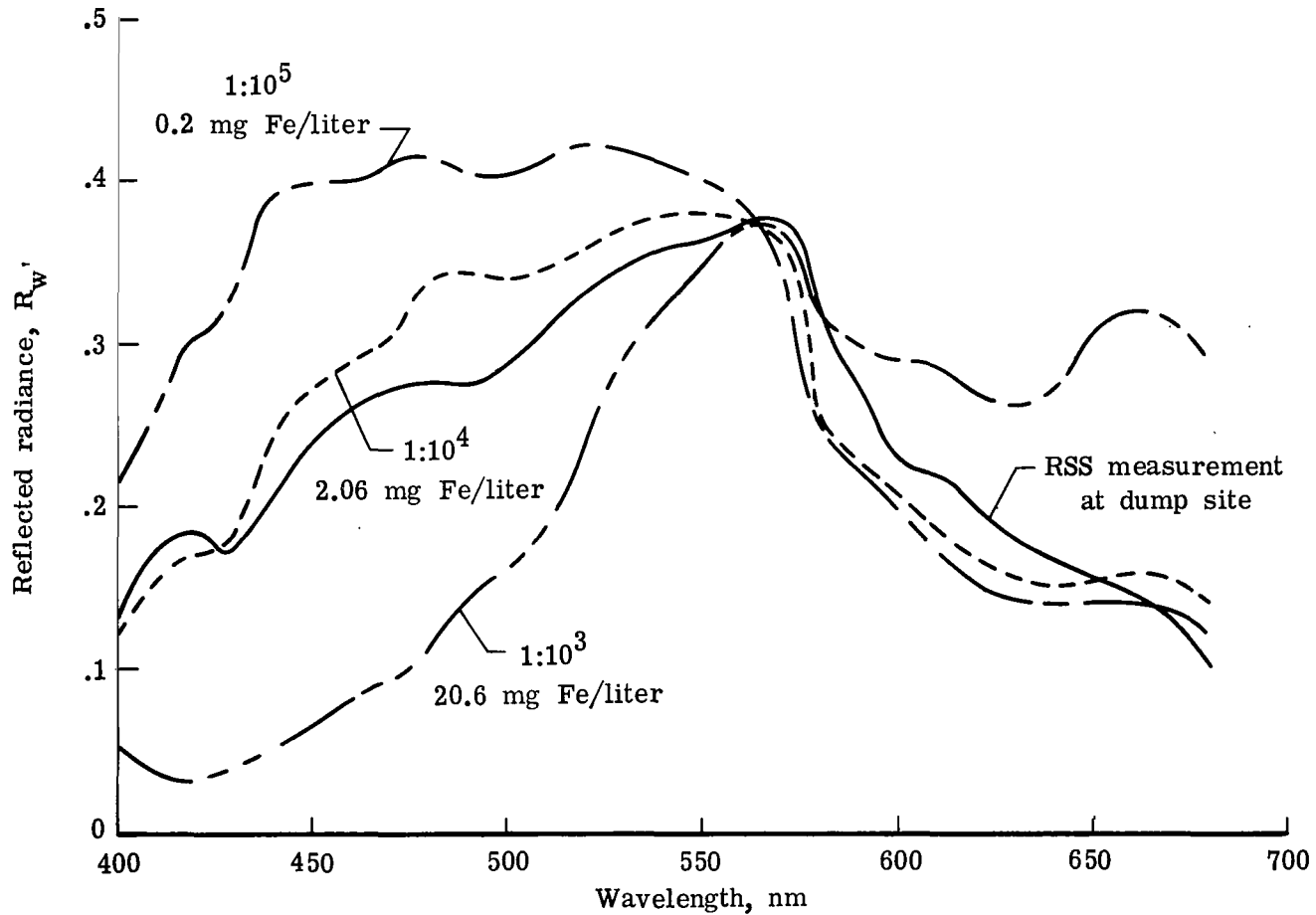
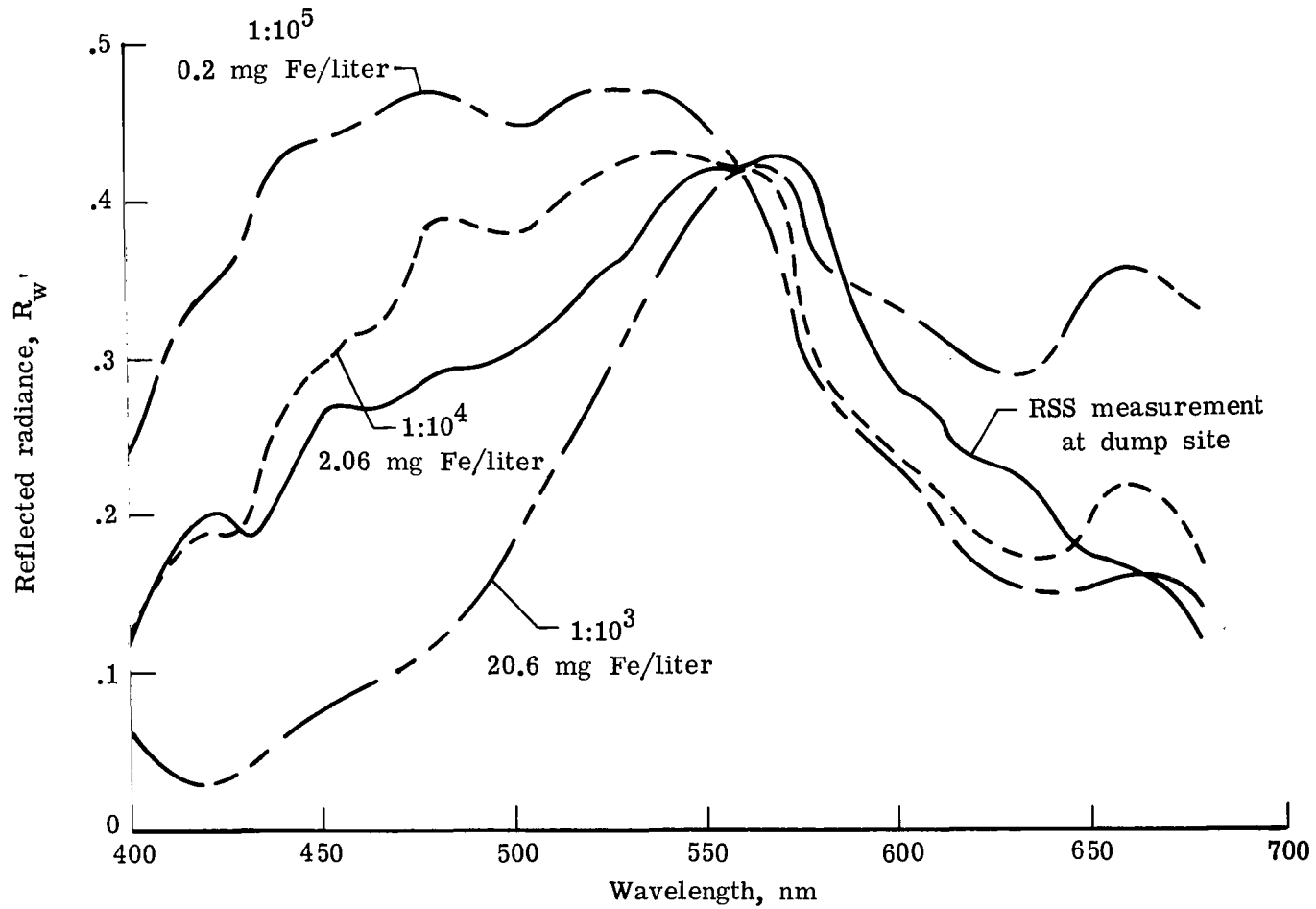


Figure 11.- Spectral transmission curves for synthetic acid waste solution (SAW-2) diluted with ocean water (SW-2) from RSS measurements using 5-cm cells. Indicated ratios are for volumetric dilutions of SAW-2 with SW-2.



(a) Plume curve is curve with second highest radiance in figure 6(a).

Figure 12.- Typical comparison of dump plume RSS data with normalized calculated reflectance for several concentrations of acid waste (AW-2) diluted with ocean water (SW-2).



(b) Plume curve is curve with highest radiance in figure 6(a).

Figure 12.- Concluded.



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