

FIG. 3. Working curve for the analysis of silicon in steel with the initial parts of the spark suppressed.

Fe II line at 3077.17Å. Arc and spark lines have here comparable intensities. In Fig. 2E the initial four microseconds only are selected. The result is that the Fe I lines are much weakened. They gain in intensity relatively to the Fe II lines if a delay is introduced at the beginning of each spark before the phototube becomes sensitive. Figures 2F–H show such a delay of increasing magnitude. The result is that the Fe II lines become increasingly weaker and have practically disappeared in Figure 2H, where the delay is about 15

microseconds. Again the weakening of the continuous background compared with the Fe I lines is noteworthy. Probably a considerable part of the remaining background is due to scattering in the spectrograph which can be reduced by proper filters.

In the equipment discussed here the onset of the phototube sensitivity is sharp, but its decline gradual. This is satisfactory for many purposes provided the sensitivity has gone down to zero before the next spark occurs. In a later version, on which work is still continuing, the sensitivity pulse of the phototube is a sharply defined square wave, the duration of which as well as the onset can be given any desired value.

In order to show the applicability of the device for spectrochemical analysis, a simple problem such as the determination of silicon in steel may be chosen. For small percentages of silicon the 2881.58 line is most suitable. Unfortunately it is severely interfered with by the strong Fe II line at 2880.76 and the Cr II line at 2881.93, so that it ordinarily cannot be used. By cutting out the beginning of the spark the Fe II line can be reduced so much in intensity that it can be used as internal standard. Figure 3 shows the working curve obtained in this way. The first rather crude realization of the device did not make it possible to cut out the Fe II line completely and use a Fe I line as standard, which otherwise would have been the better practice. With the same spectrograph and the same spark conditions Si concentrations of less than 0.3 percent could not be used.

We hope to discuss other applications in a subsequent paper.

## The Near Infrared Absorption Spectrum of Liquid Water

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The near infrared absorption spectrum of liquid water at 20°C has been reinvestigated using a PbS cell detector system. The total spectral range investigated was from 0.70 to 2.50 $\mu$ . A curve is included which shows five prominent absorption bands at 0.76, 0.97, 1.19, 1.45, and 1.94 $\mu$ ; and a table gives experimental results of water absorption at 20°C.

THE near infrared absorption spectrum of water has been the subject of several previous investigations, notably those of Hulburt and Hutchinson,<sup>1</sup> and Collins.<sup>2</sup> Hulburt and Hutchinson did their work in conjunction with an investigation of the absorption by various salts in solution. Their water absorption data cover the wavelength range from 0.704 to 1.344 microns. In 1925 Collins published water absorption data from

0.70 to 2.10 $\mu$ . He was primarily interested in the shift in position of the absorption bands as the water temperature was changed, rather than with the absorption coefficients as such. A thorough discussion of the problem has been given by Dorsey.<sup>3</sup>

However, since Collins, few results on this problem have been published. With the advent of new highly sensitive detector systems such as the PbS cells, which

<sup>1</sup> E. O. Hulburt and J. F. Hutchinson, Carnegie Institute of Washington Publication No. 260, 9 (1917).

<sup>2</sup> J. F. Collins, Phys. Rev. 26, 771 (1925).

<sup>3</sup> N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940).

make possible an extension of the wavelength range of these measurements, it was thought worth while to reopen the problem.

In this investigation, measurements were made in the spectral region 0.70 to 2.50 $\mu$ . There are five prominent water absorption bands in the near infrared which occur at 0.76, 0.97, 1.19, 1.45, and 1.94 $\mu$ . A weaker band occurs at 0.845 $\mu$ . Collins found the intensity of the bands to be enhanced when the water temperature was raised to 95°C. He further found that as the temperature of the water was increased, the position of maximum absorption was shifted to slightly shorter wavelengths. In the present investigation the water temperature was kept constant at 20°C.

A schematic diagram of the experimental arrangement is shown in Fig. 1. The dispersing unit was a Gaertner constant deviation spectrometer with quartz optics. The source was a 1000-watt G. E. projection lamp connected through a voltage stabilizer. The light was collimated and the beam stopped down before going through the water cell.

The detector system consisted of a PbS cell with power supply and amplifier. Radiation was chopped at 17 cycles per second and the photocell output was amplified, rectified, and recorded on a 5-milliamperere Esterline-Angus recorder. RMS voltage output readings were also made on a Hewlett-Packard voltmeter. The output was kept below 1 volt RMS—it had been previously established that under these conditions the response of the system was linear.

The wavelength scale of the spectrometer was calibrated by means of a mercury arc which has suitable lines in the near infrared. Accuracy of the wavelength setting was limited by the division markings on the wavelength dial. At the lower wavelengths, from 0.7 $\mu$ –1.5 $\mu$ , the settings could be made with an accuracy of about 0.001 $\mu$ , while for the longer wavelengths above 1.5 $\mu$  the accuracy was about 0.002 $\mu$ . Band widths passed by the spectrometer were kept as narrow as possible, and were in the range 0.003–0.006 $\mu$ . Measurements were made at intervals of 0.005 $\mu$  in the region 0.70 to 1.16 $\mu$ , and at intervals of 0.01 $\mu$  in all other spectral regions. For investigation the spectrum from 0.7 $\mu$  to 2.5 $\mu$  was broken up into five regions each containing one of the five prominent absorption bands mentioned above. These regions are defined in Table (I) which also gives the cell pathlength, spectrometer band width, and the absorption band position and intensity associated with each region.

Water used in the experiment was triple-distilled in an all-Pyrex system, and it appeared to be free of particles and air bubbles. Absorption data were obtained within 48 hours after final distillation and immediately after the absorption cells were filled. The cells were made of Pyrex tubing with Glyptal cemented Pyrex windows, and the lengths used varied with the region investigated; the two shortest cells consisted of quartz plates, separated by a lead gasket. Path lengths were measured

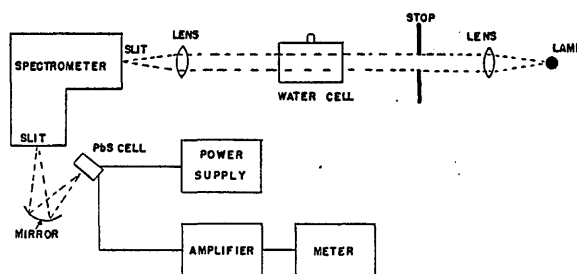


FIG. 1. Diagram of experimental arrangement.

by microscope and micrometer, and the accepted value for the path length is in each case the average of about 10 independent measurements. For all but the shortest cell, absorption measurements were made by comparing the transmissions of two water-filled cells of different length to obviate correction for reflection losses by the cell windows. A slider arrangement was provided whereby the thick and thin cells could be inserted easily into the collimated beam. In the case of the thinnest cell, where the pathlength was 0.022 cm, only one cell was used and suitable corrections were made for glass-air and glass-water reflection losses.

Scattered light in the spectrometer was reduced by means of filters. A Corning No. 2403 red filter, which did not transmit any light below 0.63 $\mu$  was used between 0.70 and 0.90 $\mu$ . A dyed Cellophane filter which did not transmit radiation below 0.88 $\mu$  was used from 0.90 to 2.50 $\mu$ .

For monochromatic radiation, the absorption coefficient,  $\alpha$ , is defined by the relationship

$$I = I_0 e^{-\alpha x},$$

where  $I_0$  is the original intensity of radiation and  $I$  the intensity after passing through  $x$  cm of water. Since the spectral transmission  $T$  is defined by

$$T = I/I_0,$$

the absorption coefficient may be written as

$$\alpha = (1/x) \ln(1/T).$$

Each absorption coefficient plotted in Fig. 2 is the average of at least three independent measurements. The independent measurements deviated by less than 0.002  $\text{cm}^{-1}$  from the average plotted value for each

TABLE I. Water absorption at 20°C.

Wavelength	Water path length (cm)	Spectrometer band width ( $\mu$ )	Wavelength of max. absorption	Absorption coefficient at max. absorption ( $\text{cm}^{-1}$ )
0.70–0.90	12.972	0.006	0.76	0.026
0.90–1.15	1.993	0.003	0.97	0.46
1.15–1.35	0.987	0.003	1.19	1.05
1.35–1.80	0.090	0.003	1.45	26.0
1.80–2.50	0.022	0.004	1.94	114.0

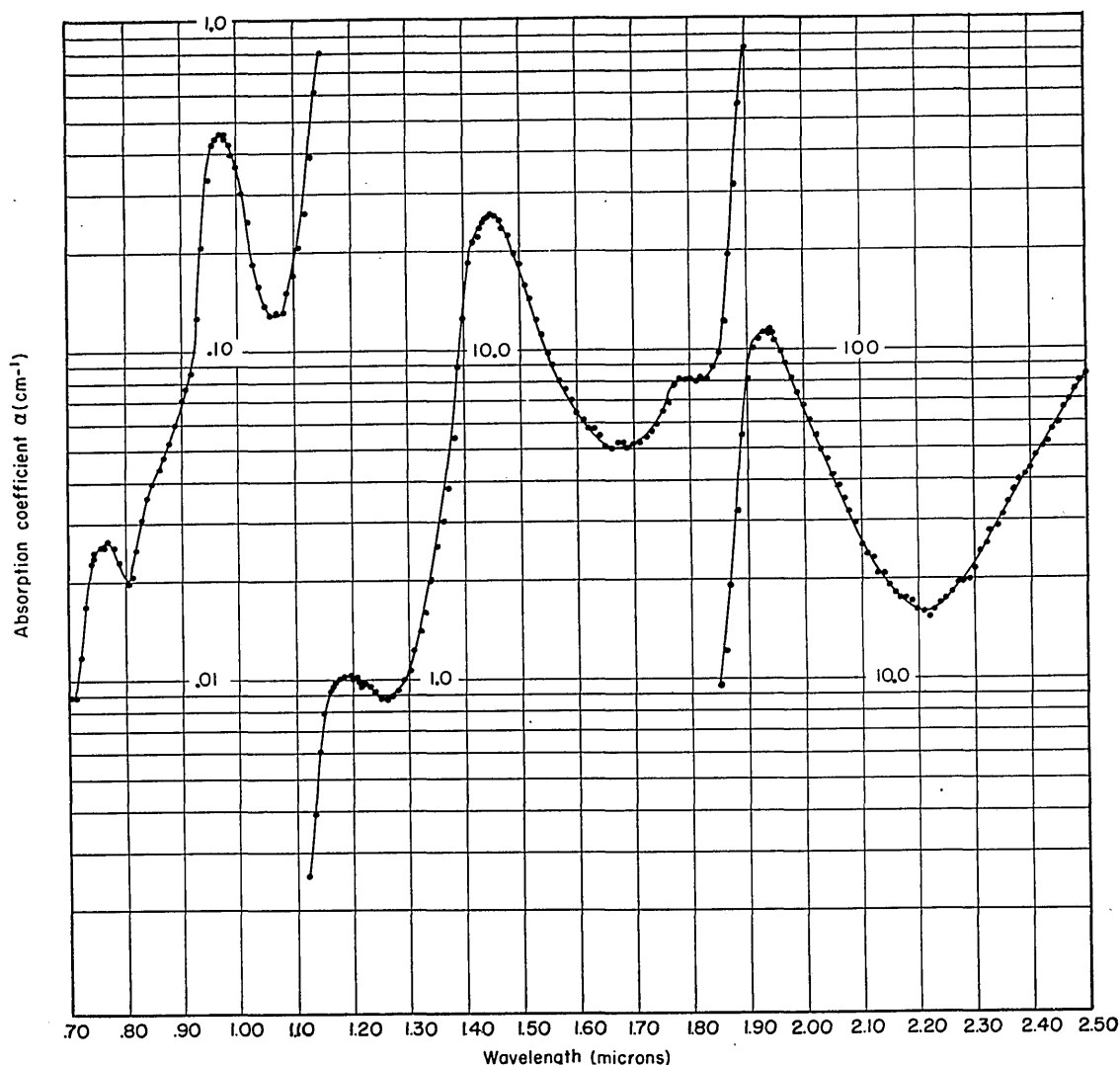


FIG. 2. Absorption coefficients of water at 20°C.

wavelength in the region from  $0.70\mu$  to  $0.90\mu$ . From  $0.90\mu$  to  $2.5\mu$ , the mean deviation for each plotted average value was less than 5 percent of the average value.

Figure 2 shows absorption coefficients of water at 20°C for the spectral region  $0.70\mu$  to  $2.50\mu$ . The regions of maximum absorption occur at  $0.76$ ,  $0.97$ ,  $1.19$ ,  $1.45$ , and  $1.94\mu$ . A weaker band is evident by the shoulder on the curve at about  $0.85\mu$ . Collins found this band to be more pronounced and enhanced when the water temperature was raised to 95°C.

The absorption coefficients shown in Fig. 2 are lower by 5 percent than those obtained by Hulburt and

Hutchinson for the wavelength interval  $0.7\mu$  to  $1.34\mu$ . The present measurements were made with a resolution of  $0.003\mu$  to  $0.006\mu$ , whereas those of Hulburt and Hutchinson were made with a resolution of  $0.002\mu$ . The present values agree to within 2 percent with those obtained by Collins except in the spectral interval  $1.6\mu$  to  $1.9\mu$ , where the present values of  $\alpha$  are 10 percent lower. A shoulder on the  $1.94\mu$  absorption band was found at  $1.80\mu$ , which accounts for the lower  $\alpha$  in this region. Collins' resolution was  $0.005\mu$  to  $0.015\mu$ . The present data show that beyond  $2.1\mu$ ,  $\alpha$  drops to a minimum at  $2.2\mu$ , then increases steadily out to  $2.5\mu$ , the long wavelength limit of the present measurements.