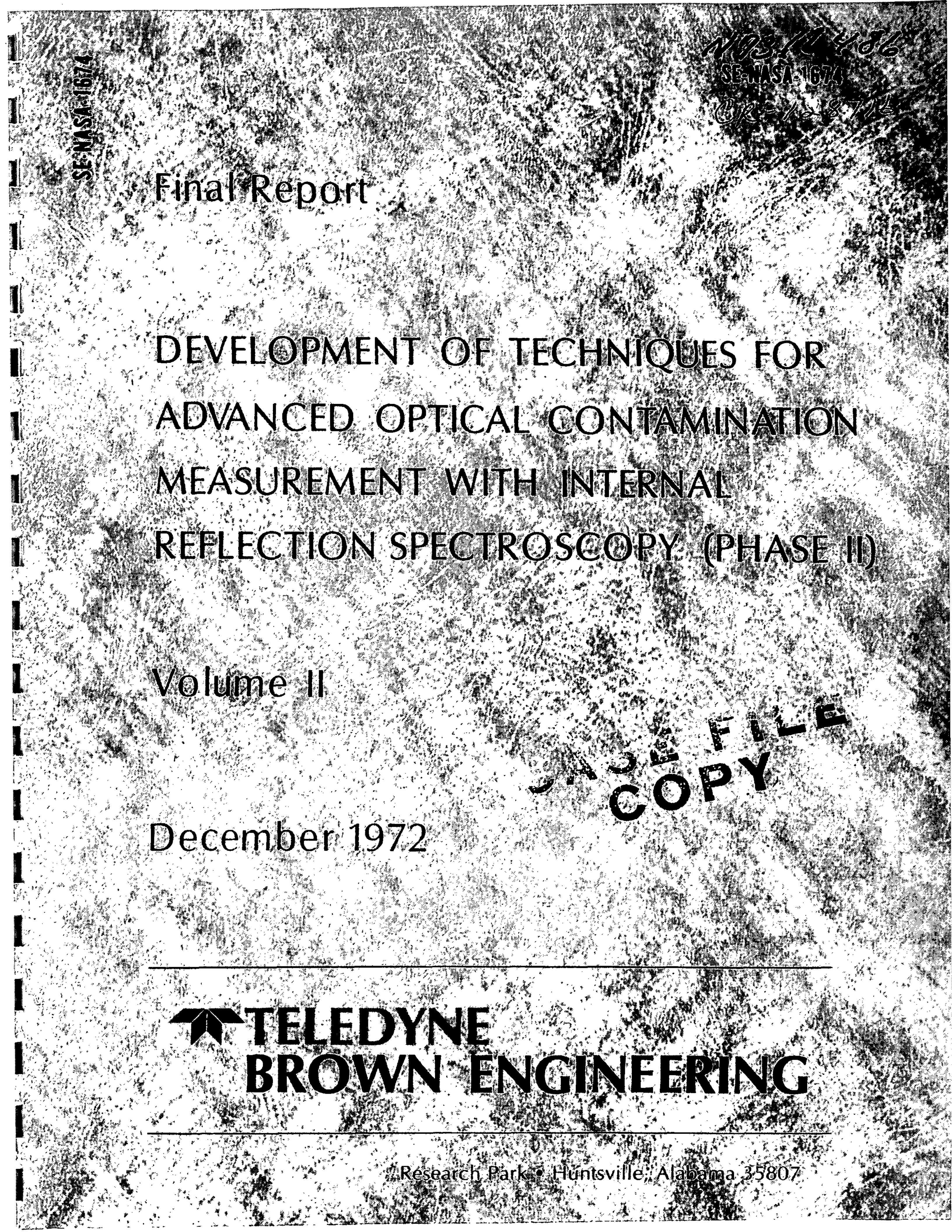

Final Report

DEVELOPMENT OF TECHNIQUES FOR ADVANCED OPTICAL CONTAMINATION MEASUREMENT WITH INTERNAL REFLECTION SPECTROSCOPY (PHASE II)

Volume II

December 1972

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VOLUME II

DEVELOPMENT OF TECHNIQUES FOR ADVANCED OPTICAL CONTAMINATION MEASUREMENT WITH INTERNAL REFLECTION SPECTROSCOPY (PHASE II)

By

J. D. Hayes

December 1972

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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HUNTSVILLE, ALABAMA

EXECUTIVE SUMMARY

The feasibility of monitoring volatile contaminants in a large space simulation chamber using techniques of internal reflection spectroscopy has been demonstrated analytically and experimentally. The analytical results of the Phase I study are documented in Volume I of this report and the experimental results obtained in the Phase II study are reported in Volume II. The infrared spectral region was selected as the operational spectral range in order to provide unique identification of the contaminants along with sufficient sensitivity to detect trace contaminant concentrations. It was determined theoretically that a monolayer of the contaminants of interest could be detected and identified using optimized experimental procedures. This ability was verified experimentally. Procedures were developed to correct the attenuated total reflectance spectra for thick sample distortion. However, by using two different element designs the need for such correction can be avoided.

The analysis of spectra of multicomponent samples was considered analytically and procedures were selected to determine both qualitatively and quantitatively the contents of such samples. Experimentally, one multicomponent sample was analyzed and the results were accurate to within ±50 percent overall.

To provide sufficient sensitivity for the variety of experimental conditions anticipated, the use of two different internal reflection elements is recommended. For normal thin film (>200 Å) measurements and for thick film or bulk sample measurements, a 35-degree, 26 reflection germanium element is recommended. For high sensitivity measurements for thin films between 20 Å and approximately 6,000 Å,

a 30-degree, 46 reflection KRS-5 element is recommended. Some hardware considerations for an ATR real-time contaminant monitor are also discussed in Volume II.

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1. INTRODUCTION

The feasibility of using Attenuated Total Reflectance (ATR) techniques to identify qualitatively and quantitatively six specific components known or suspected to prevail in the space simulation chambers at the National Aeronautics and Space Administration, Manned Spacecraft Center (NASA-MSC) was shown analytically in Volume I of this report.

This portion of the report, Volume II, describes the experimental work that was performed to verify the analytical results. Spectra of individual contaminants are presented as well as spectra of mixtures and figures exhibiting the effects of film thickness on ATR spectra.

The method of approach was to demonstrate the feasibility, experimentally, of using ATR techniques to monitor and identify contaminants in real time. Detailed calibration spectra were made for three selected concentrations (film thickness) for two contaminants and for one concentration for all other contaminants.

2. INTERNAL REFLECTION ELEMENT FABRICATION

Three element designs were selected for element fabrication based on the Phase I study results. These included a 46 reflection KRS-5 element for operation at 30 degrees, a 26 reflection germanium element for operation at 35 degrees, and a 26 reflection germanium element for operation at 40 degrees in conjunction with KRS-5 plates as the third optical medium.

The IREs were designed for use with converging radiation from a monochromator for which the half-angle of convergence of the incident beam is approximately 2 to 5 degrees. However, the entrance and exit apertures of the crystals were truncated to allow use in more highly convergent incident beams if desired. The parallelepiped style was selected to provide room for the auxiliary beam forming and collecting optics. The physical dimensions of the crystals were selected to satisfy three primary considerations simultaneously; first, the actual number of internal reflections of the final design should be approximately the same as the proposed number; second, the entrance aperture should be large enough to fully accommodate the converging incident radiation beam (2 to 5 degree half-angle) assuming a maximum monochromator exit slit width of 2 millimeters; and third, the length of the crystal should be such that if the monochromator exit slit were imaged at the center of the IRE, the beam exiting the IRE would not be partially blocked by the exit aperture of the IRE. Because most grating monochromators are astigmatic, the width of the IRE was set at 2 centimeters in order to reduce the requirements on the beam forming optics.

The actual fabrication of the IREs was performed by Harrick Scientific Corporation, Ossing, New York. The two internally reflecting faces of the IRE were specified to be parallel to within one minute of angle. The angle of incidence was to be within 0.5 degree of the selected angle.

Although it is possible to measure each of the parameters specified individually, the most important measure of an IRE is its actual performance. The IREs delivered to Teledyne Brown Engineering (TBE) were checked out as follows. First, the physical dimensions of each IRE were checked. Second, each IRE was mounted on an optical bench and the angle of the bevel face was measured utilizing a helium-neon laser reflectance technique. Finally, the wavelength dependence of the transmittance of the IRE was measured to check finish quality.

The elements were all found to be of high quality and well within specified tolerances.

3. SPECTRAL RESPONSE MEASUREMENTS

3.1 INDIVIDUAL CONTAMINANT SPECTRA

The spectral response of each of the individual contaminants of interest was measured for several contaminant thicknesses using the different IREs. Several methods of depositing the contaminants were tried. The most desirable method was to outgas or heat to volatility the contaminant in a vacuum chamber and to allow the volatile contaminant to deposit on the IRE, monitoring the thickness of the deposit with a quartz crystal microbalance (QCM) located adjacent to the IRE. Although it was possible to get good contaminant films by this method, it was impossible to determine the film thickness on the IRE for two reasons.

First, it was obvious from visual observations during deposition that the sticking coefficient of the contaminant/IRE interface was much greater than that of the contaminant/QCM interface. Second, the QCM exhibited a self-cleaning process when maintained operational during the deposition. This was demonstrated by establishing a constant evaporation rate, measuring the mass deposited during a specified time interval with the oscillator on, and then measuring the mass deposited after an equal time interval with the oscillator off during deposition.

The deposited mass was consistently greater for the periods when the oscillator was off. Because of the uncertainties in film thickness for samples deposited by the above techniques, it was decided to apply the contaminants from standard acetone or carbon tetrachloride solutions. Standard solutions of 0.01, 0.1, 1.0, and 10.0 percent contaminant by volume were prepared for each of the contaminants of interest except DC-11. Solutions of 0.01, 0.1, and 1.0 percent DC-11 by weight were prepared, since DC-11 is normally a semi-solid. Acetone is a poor solvent for DC-11 so that only CCl_4 solutions of DC-11 were prepared.

A known quantity of the desired solution was dispersed on each reflecting face of the IRE and the solvent allowed to evaporate before the spectra were recorded. The thickness of the deposited film was calculated from the quantity of solution dispersed and the area of the IRE face, assuming a film of uniform thickness. The mass of contaminant deposited was checked by depositing an equal quantity of contaminant on a QCM crystal and measuring the frequency shift after solvent evaporation.

Figures 1 through 7 show ATR spectra of the individual contaminants of interest as measured with a 45-degree KRS-5 IRE, in conjunction with a Beckman filter wheel monochromator and a highly convergent (half-angle approximately 20 degrees) incident radiation beam. The incident radiation was unpolarized. For all the measurements except for the mixtures, the 3M Black Velvet coating components were measured separately and after the carbon pigment had been removed from the component. This was done because the Black Velvet coating is an epoxy coating that would ruin the IREs if allowed to cure. The spectra in Figures 1 through 7 are for films approximately 0.6 micrometer thick on each face of the IRE.

Typical individual spectra of the contaminants on the 35-degree germanium and on the 30-degree KRS-5 IREs are shown in Figures 8 through 14. These spectra were recorded using a McPherson Model 218 grating monochromator with 2-millimeter entrance and exit slits, a converging incident radiation beam of 5-degree half-angle, with the incident radiation polarized parallel to the plane of incidence of the internal reflections. The films for these spectra were approximately 0.2 micrometer thick. In general, the spectra taken with the latter IREs show higher resolution and greater sensitivity than do those taken with the 45-degree KRS-5 IRE in a highly convergent radiation beam.

Table 1 summarizes the band minima positions for the contaminants of interest. This table and the individual contaminant spectra are useful in identifying the contaminants present.

3.2 CONTAMINANT MIXTURE SPECTRA

A mixture of 0.2 percent DC-705, 0.2 percent Sun vis 706, 0.2 percent Houghto Saf 1120, and 0.4 percent 3M Black Velvet was prepared and spectra recorded using the 45-degree KRS-5, the 30-degree KRS-5, and the 35-degree germanium IREs, as before. These spectra are shown in Figures 15, 16, and 17. Film thickness on the 45-degree KRS-5 IRE was approximately 0.4 micrometer, while that for the other two spectra was approximately 0.2 micrometer. The improved detail for the 30-degree KRS-5 and the 35-degree germanium IREs over the standard 45-degree KRS-5 IRE is readily apparent. The Houghto Saf 1120 contaminant has so many strong absorption bands that the spectra is difficult to analyze quantitatively. Qualitatively, the band assignments are as follows:

BAND (μm)	CONTAMINANT
3.4	Sun vis 706, Houghto Saf 1120, DC-705. 3M Component I
5.75 to 5.8	3M Components I and II
6.3	DC-705, Houghto Saf 1120
6.7	Houghto Saf 1120
6.85 to 7.0	DC-705, Houghto Saf 1120, 3M Component I
7.2 to 7.3	3M Component II, Sun vis 706
7.7	Houghto Saf 1120
7.95	DC-705, 3M Component II
8.3 to 8.7	3M Components I and II, Houghto Saf 1120
8.95	DC-705, Houghto Saf 1120, 3M Component II
9.3	Houghto Saf 1120
9.4 to 9.6	DC-705
10.4	Houghto Saf 1120

TABLE 1. CONTAMINANT BAND POSITIONS

CONTAMINANT	BAND MINIMA POSITIONS (μm) AND RELATIVE BOND STRENGTHS																					
DC-704	3.25 (M)	3.4 (M)		4.3 (W)	5.2 (W)	5.5 (W)		6.3 (W)			7.0 (S)		8.0 (VS)		9.0 (VS)		9.7 (VS)		11.8 (S)	12.8 (VS)		13.9 (S)
DC-705	3.3 (M)	3.4 (W/M)						6.3 (W)			7.0 (S)		8.0 (VS)		9.0 (VS)		9.5 (VS)			12.8 (VS)		13.8 (S)
Houghto SAF 1120	3.3 (M)	3.4 (VS)			5.2 (M)			6.3 (S)	6.7 (S)	6.9 (S)		7.7 (S)		8.5 (S)	9.0 (W)	9.2 (S)	9.7 (M)	10.4 (VS)	12.0 (M)		13.0 (S)	
Sun vis 706		3.45 (VS)		4.3 (W)						6.9 (S)		7.3 (S)		8.7 (W)								14.0 (M)
3M Component I		3.45 (VS)	3.5 (S)				5.75 (VS)			6.85 (M)		7.25 (W)		8.65 (S)					12.0 (W)			
3M Component II	2.9 (M)	3.4 (S)					5.8 (VS)					7.2 (M)	7.9 (VS)	8.5 (S)	9.0 (W)	9.4 (M)		10.3 (W)	11.3 (W)		13.5 (W)	
DC-11		3.4 (S)						6.3 (W)			7.0 (S)		8.0 (S)		9.0 (VS)		9.5 (VS)		11.5 (S)	12.5 (VS)		

(W) - Weak
(M) - Moderate
(S) - Strong
(VS) - Very Strong

Quantitatively, the analysis proceeded as follows. The 10.4-micrometer band of Houghto Saf 1120 indicated a concentration equivalent to 0.12 percent. The 9.3-micrometer band gave an indication of 0.28 percent, and the 6.7-micrometer band indicated a concentration equivalent of 0.18 percent Houghto Saf. The actual equivalent concentration was 0.2 percent (0.1 percent corresponds to approximately 200 Å film thickness).

Next, the 5.75-micrometer band was analyzed and indicated a concentration of 0.34 percent 3M components I and II. The actual concentration was 0.4 percent.

Next, the 8.95-micrometer band was analyzed for DC-705 and indicated a concentration of 0.28 percent. The actual concentration was 0.2 percent.

Finally, the 3.4-micrometer band was analyzed for Sun vis 706, after subtracting out the DC-705, the Houghto Saf 1120 and the 3M component I contributions. The indicated concentration was 0.31 percent; the actual concentration was 0.2 percent.

From this single spectrum, it appears that it will be feasible to obtain quantitative results on contaminant concentrations. The primary masking contaminant was the Houghto Saf 1120. It is believed that more accurate results could have been obtained if the Houghto Saf 1120 had been omitted.

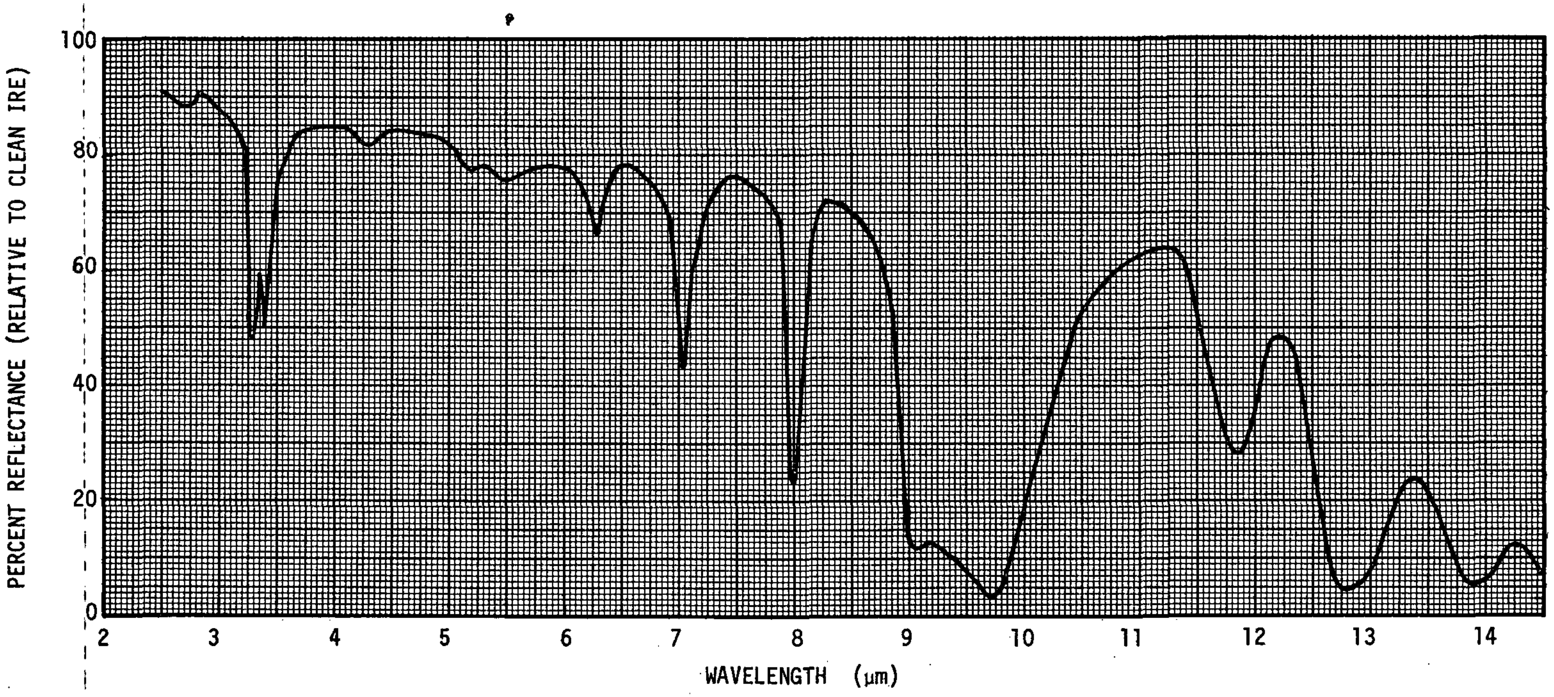

FIGURE 1. DC-704 ON 45-DEGREE KRS-5 IRE

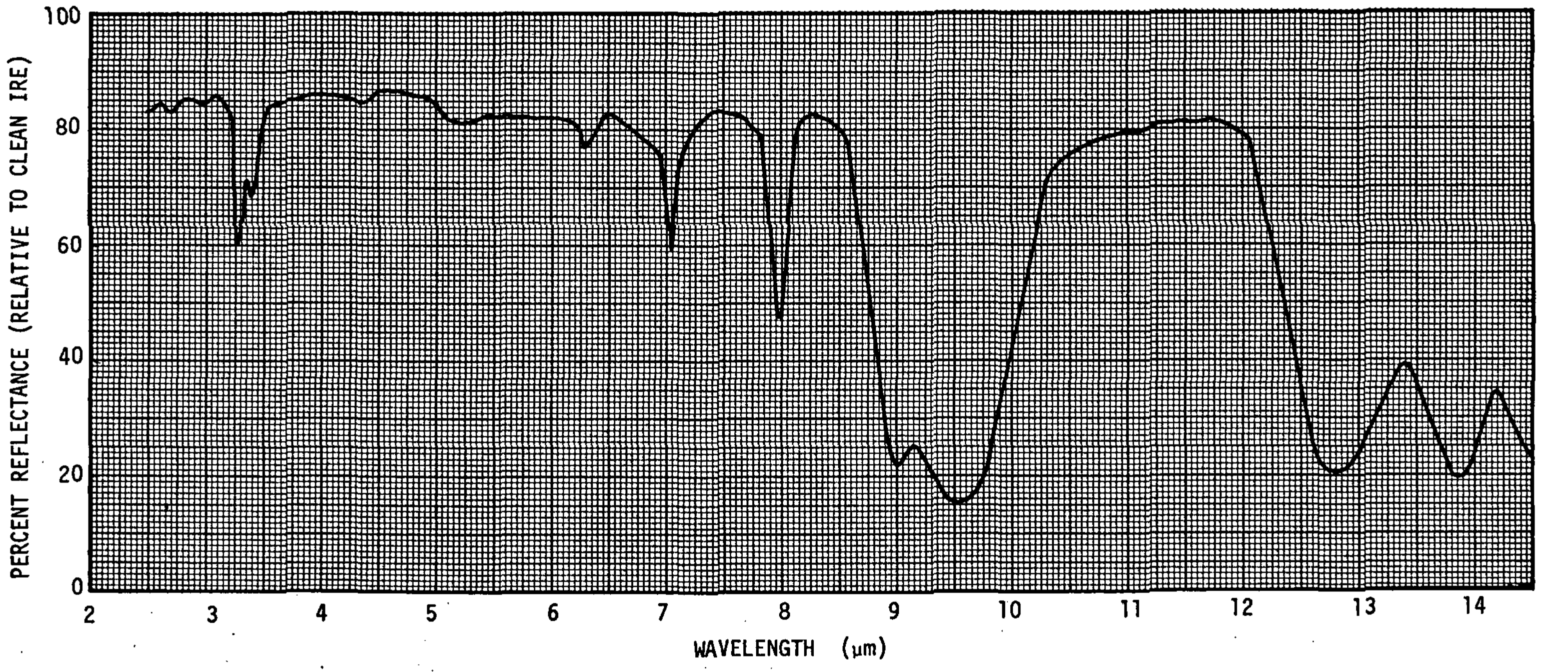

FIGURE 2. DC-705 ON 45-DEGREE KRS-5 IRE

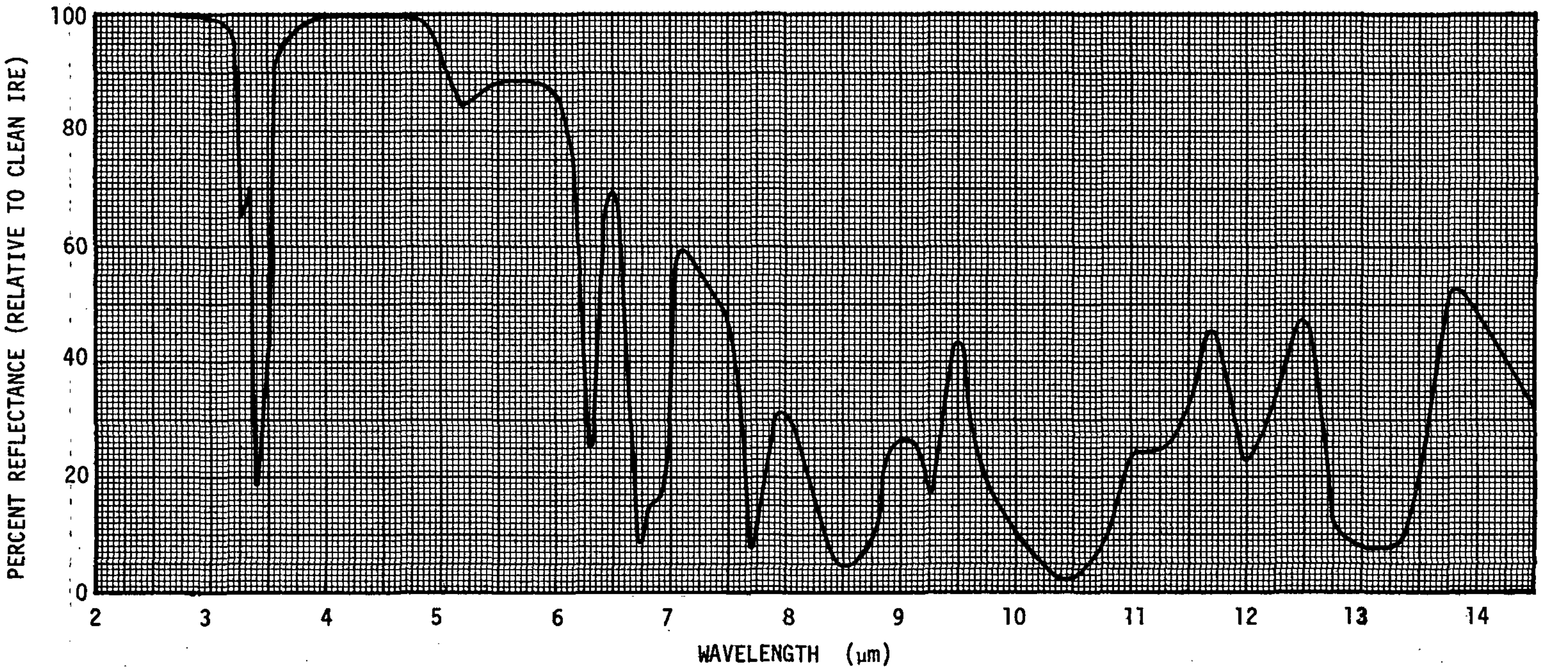

FIGURE 3. HOUGHTO SAF 1120 ON 45-DEGREE KRS-5 IRE

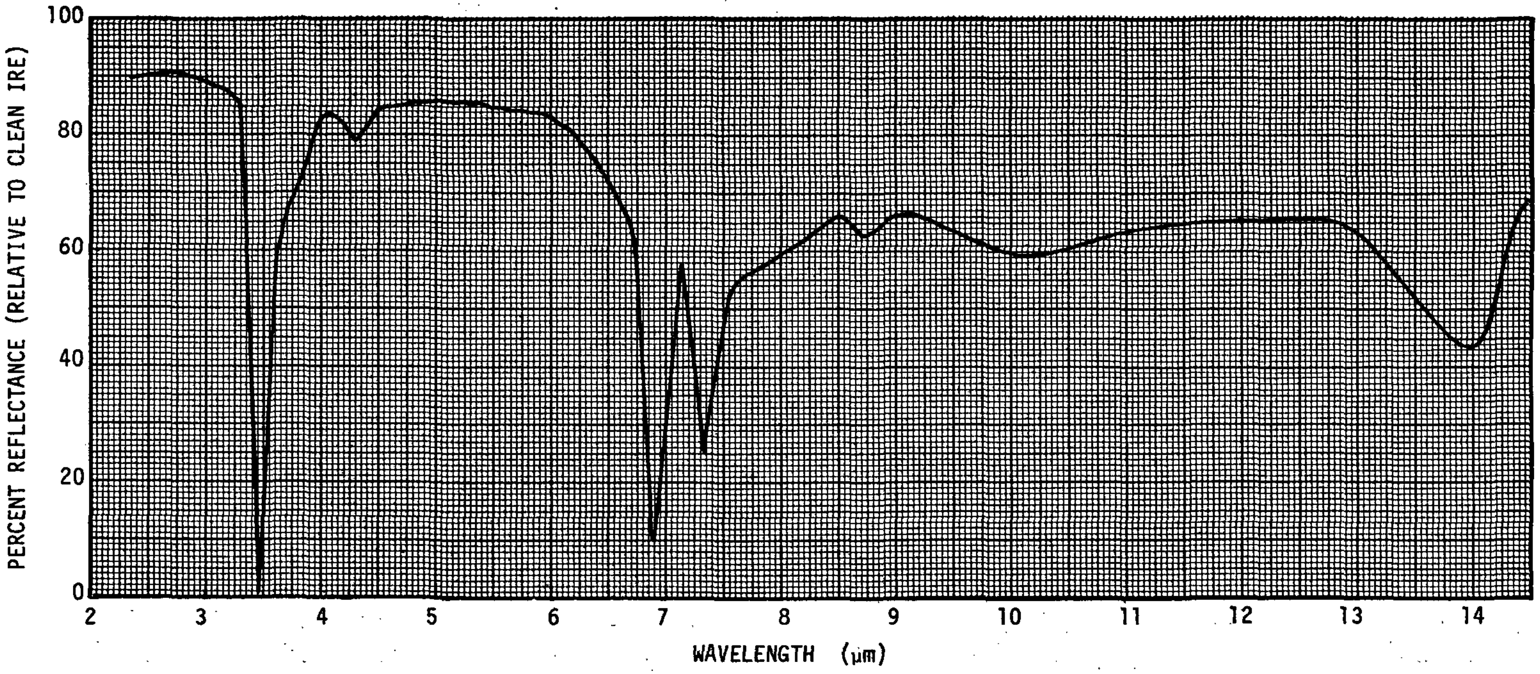

FIGURE 4. SUN VIS 706 ON 45-DEGREE KRS-5 IRE

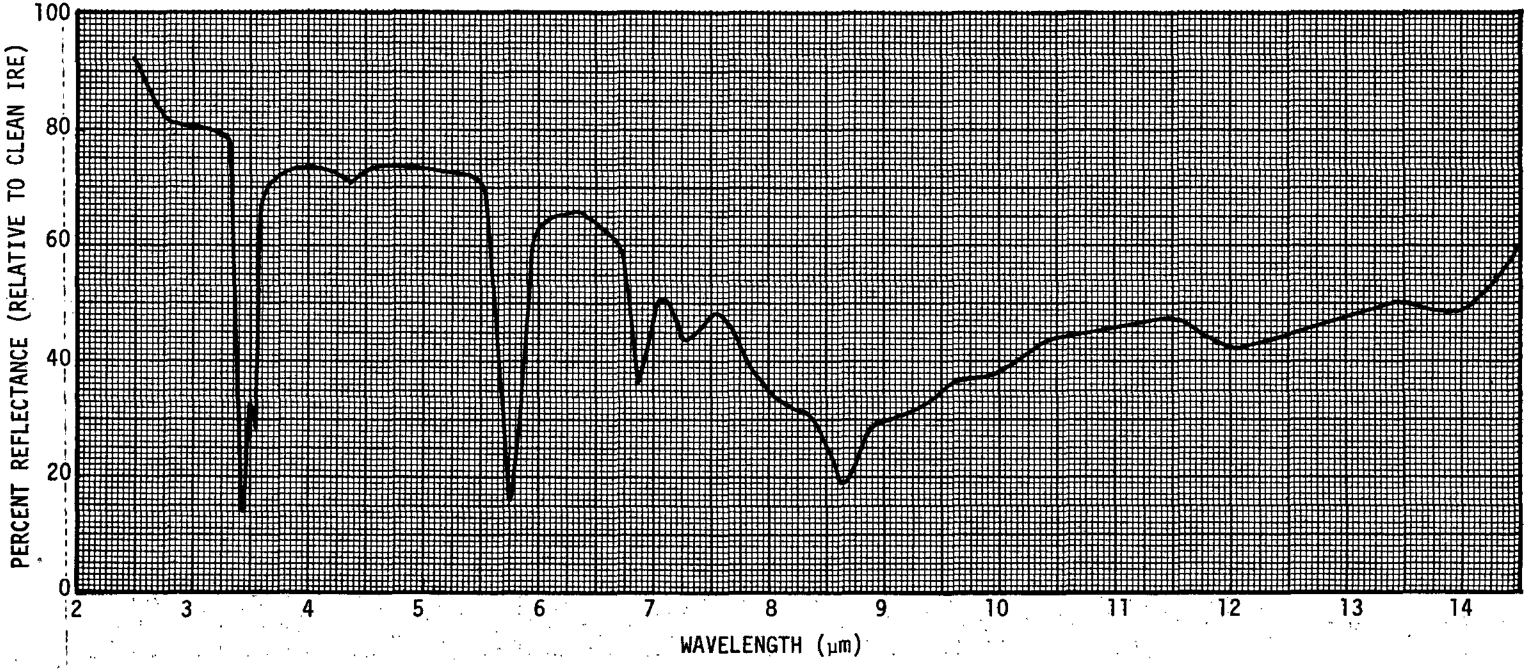

FIGURE 5. 3M BLACK VELVET 401-C10 (COMPONENT I) ON 45-DEGREE KRS-5 IRE

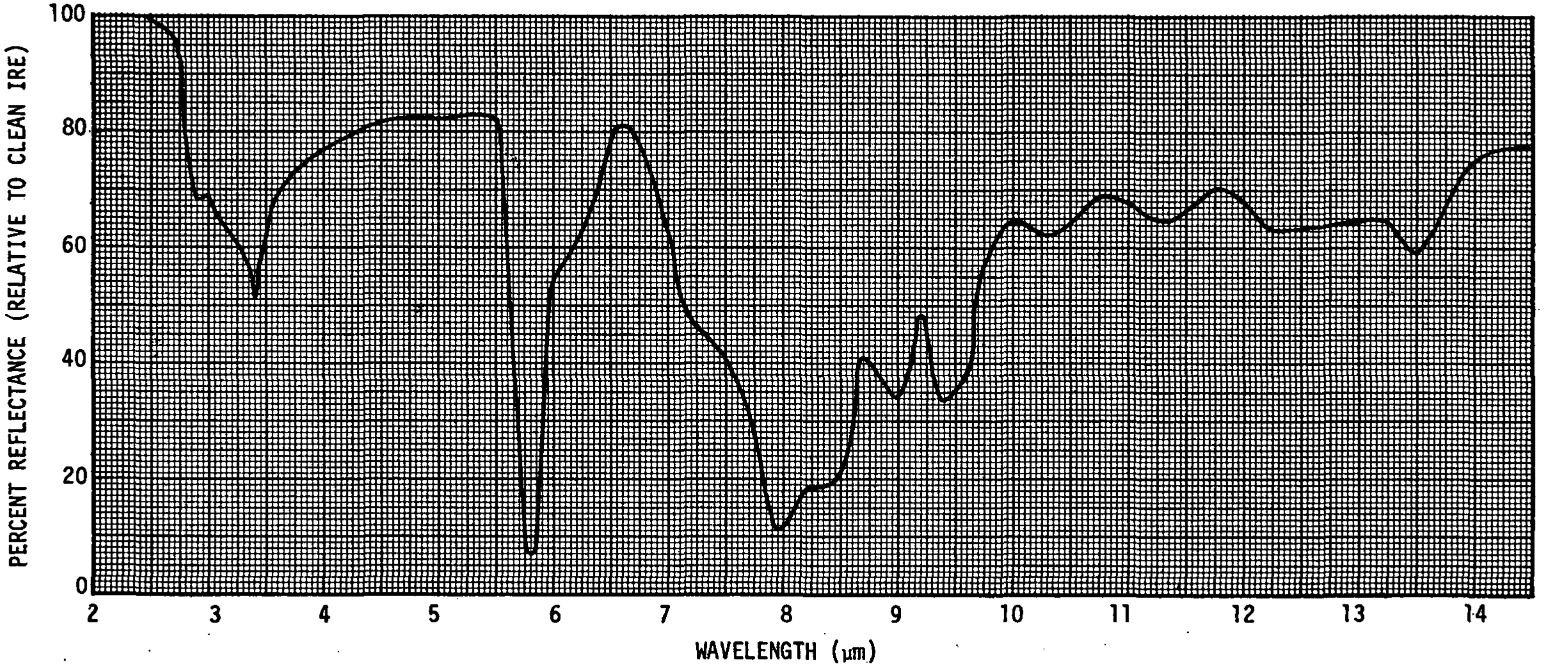

FIGURE 6. 3M BLACK VELVET 401 SERIES (COMPONENT II) ON 45-DEGREE KRS-5 IRE

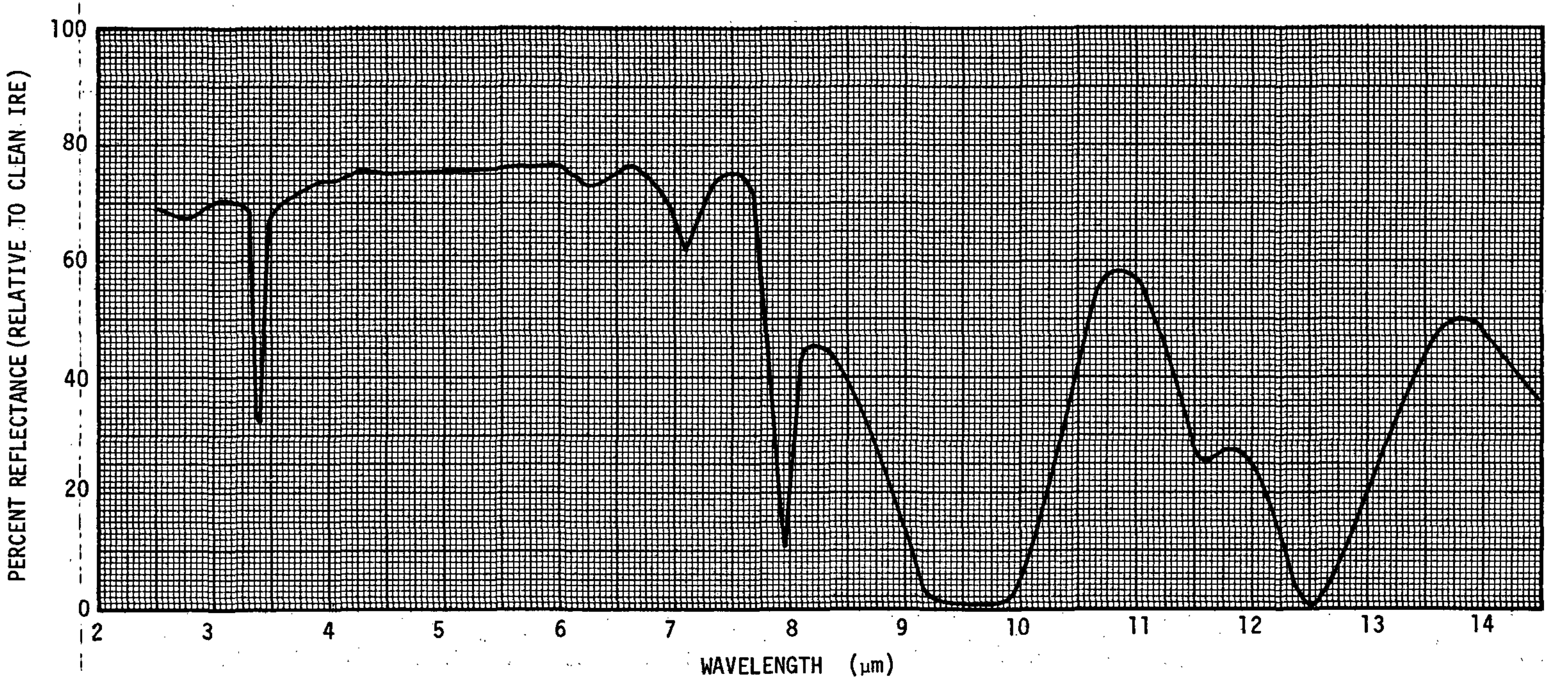

FIGURE 7. DC-11 ON 45-DEGREE KRS-5 IRE

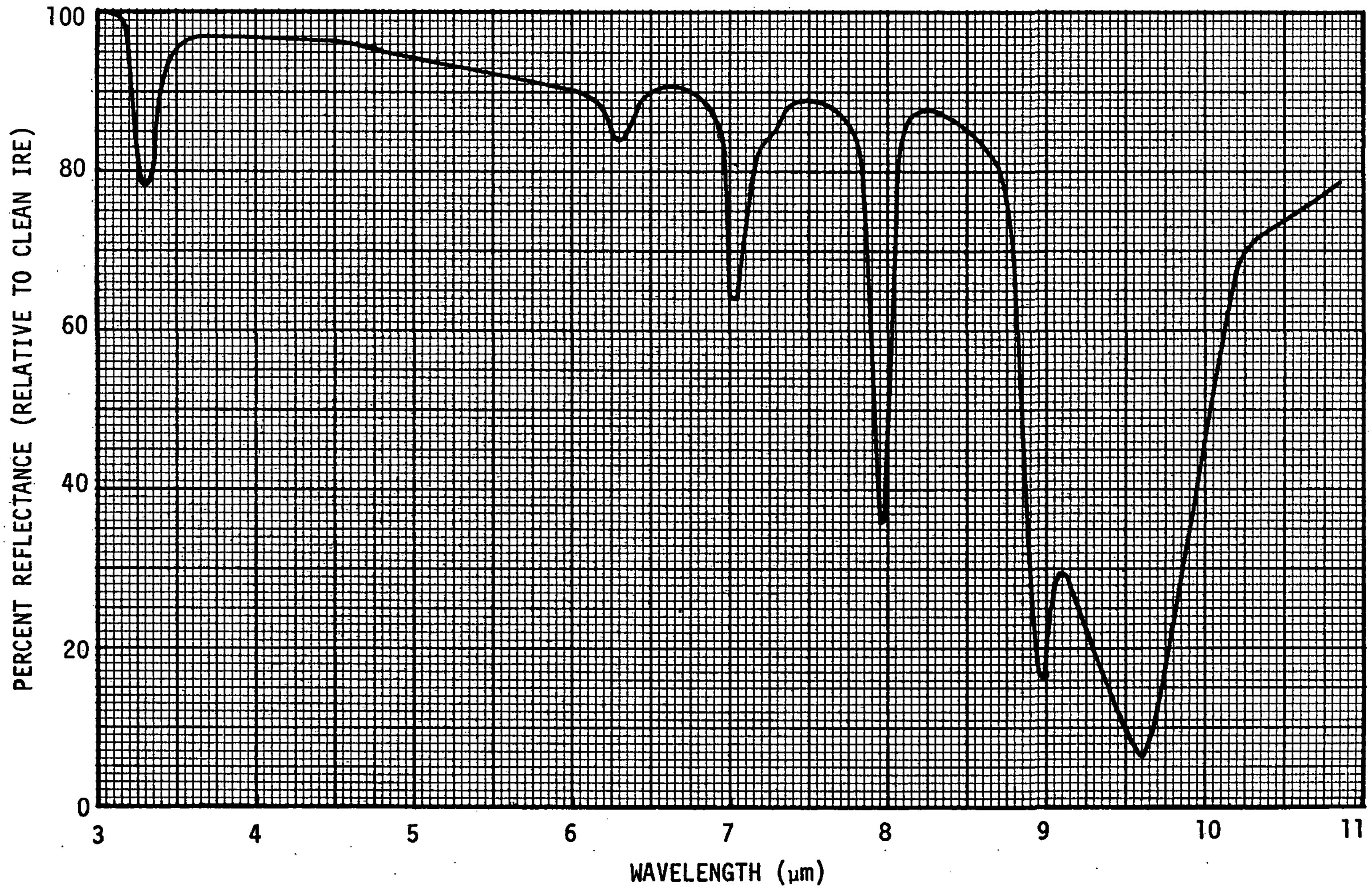

FIGURE 8. DC-704 ON 35-DEGREE GERMANIUM IRE

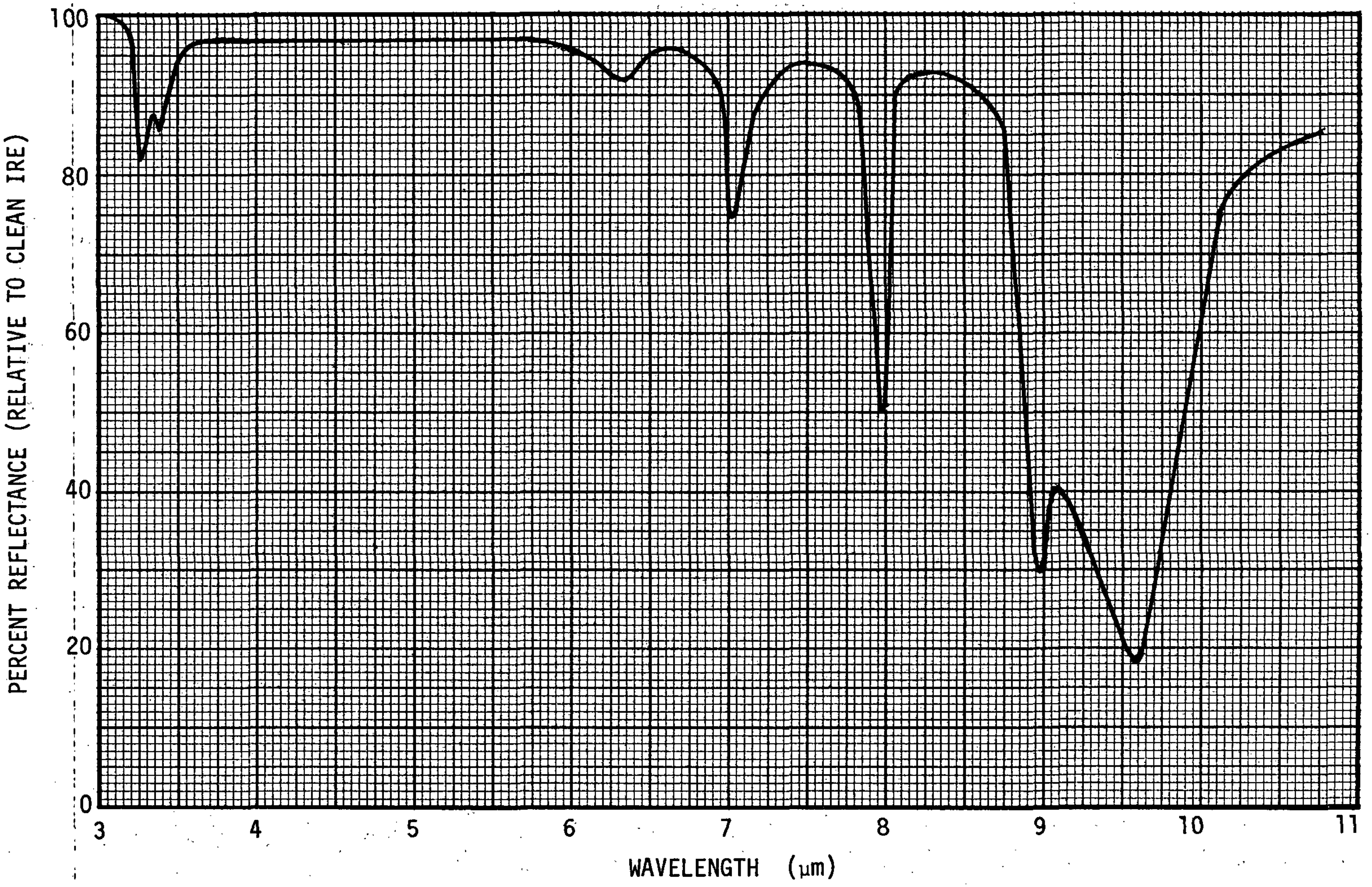

FIGURE 9. DC-705 ON 35-DEGREE GERMANIUM IRE

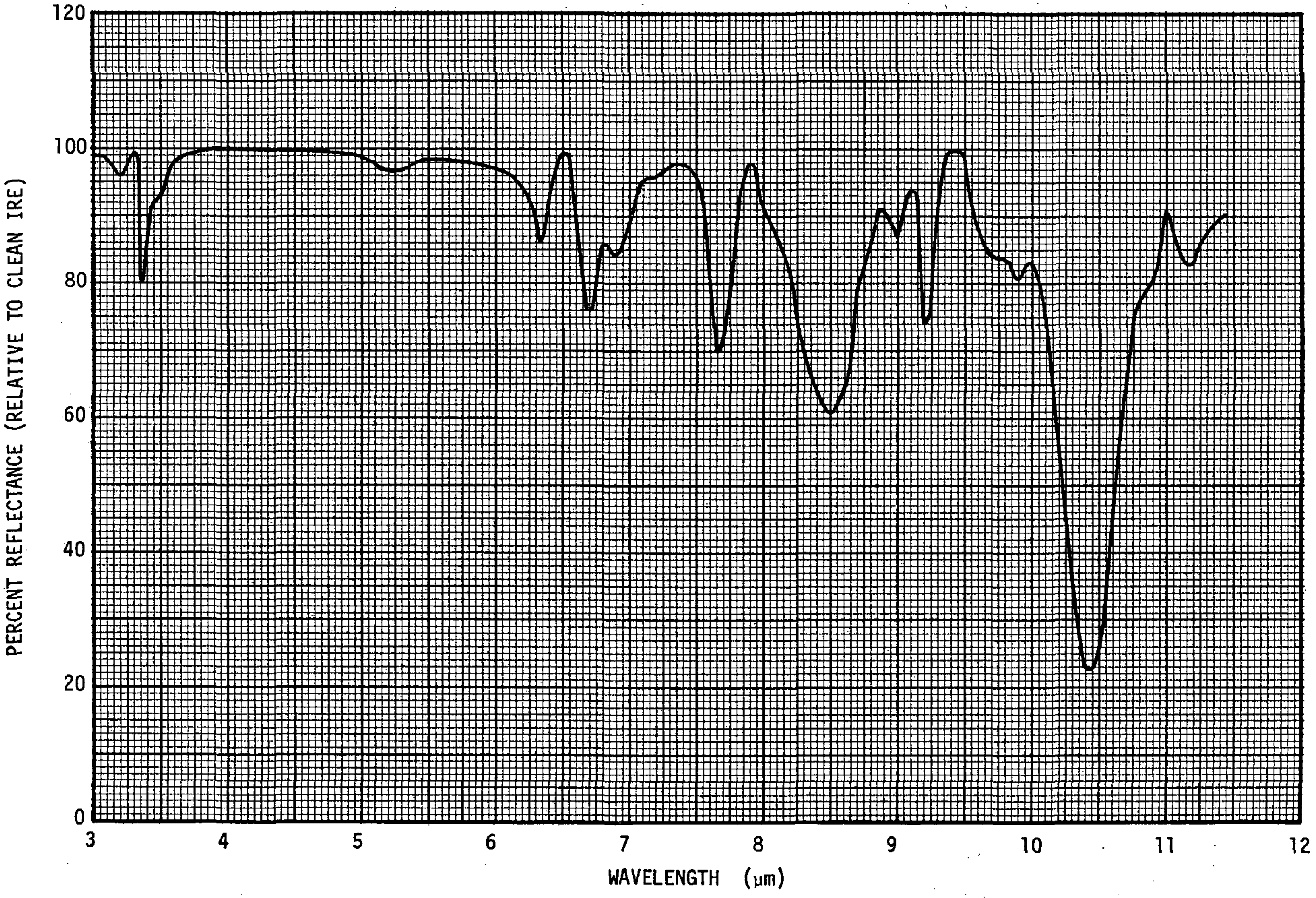

FIGURE 10. HOUGHTO SAF 1120 ON 35-DEGREE GERMANIUM IRE

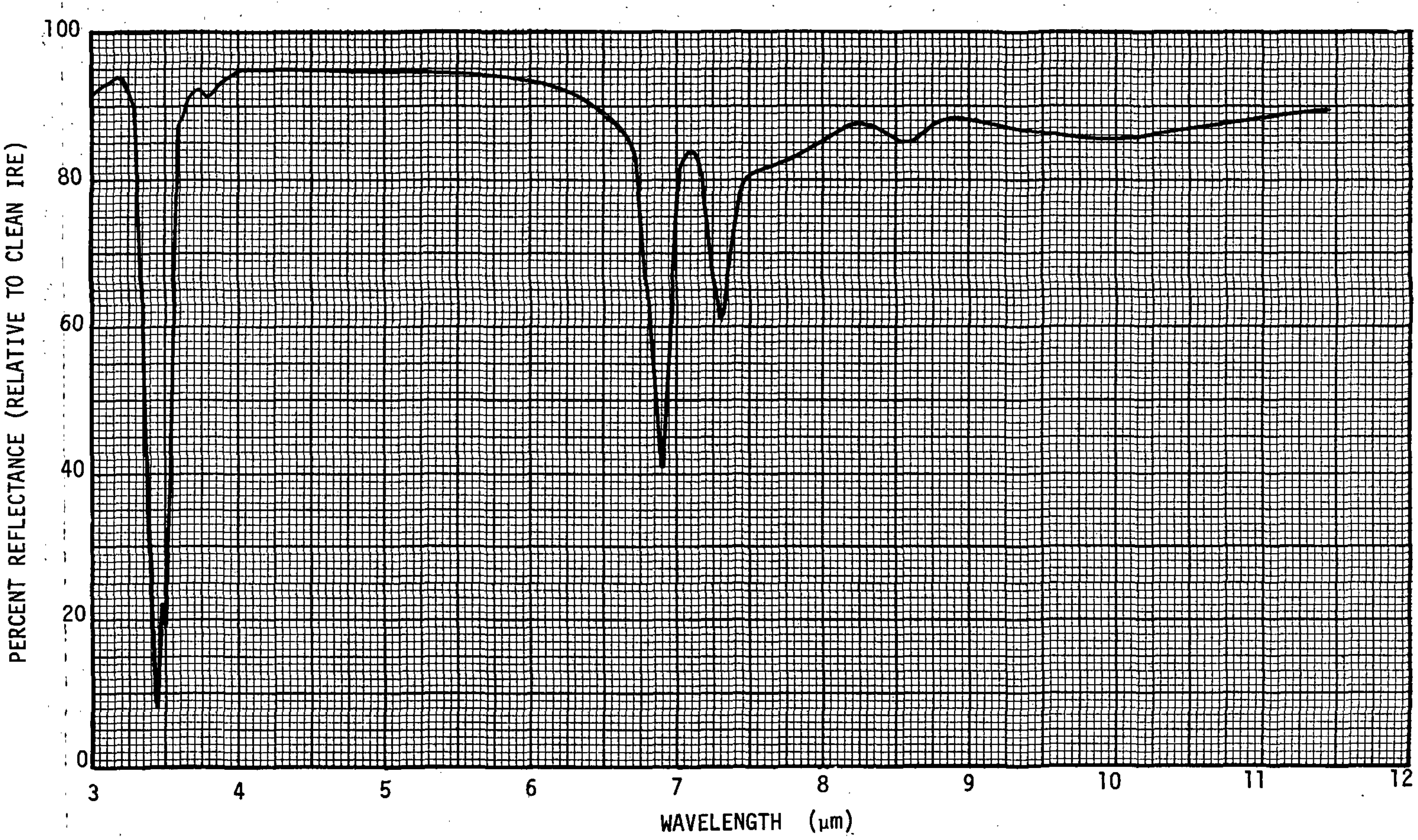

FIGURE 11. SUN VIS 706 ON 35-DEGREE GERMANIUM IRE

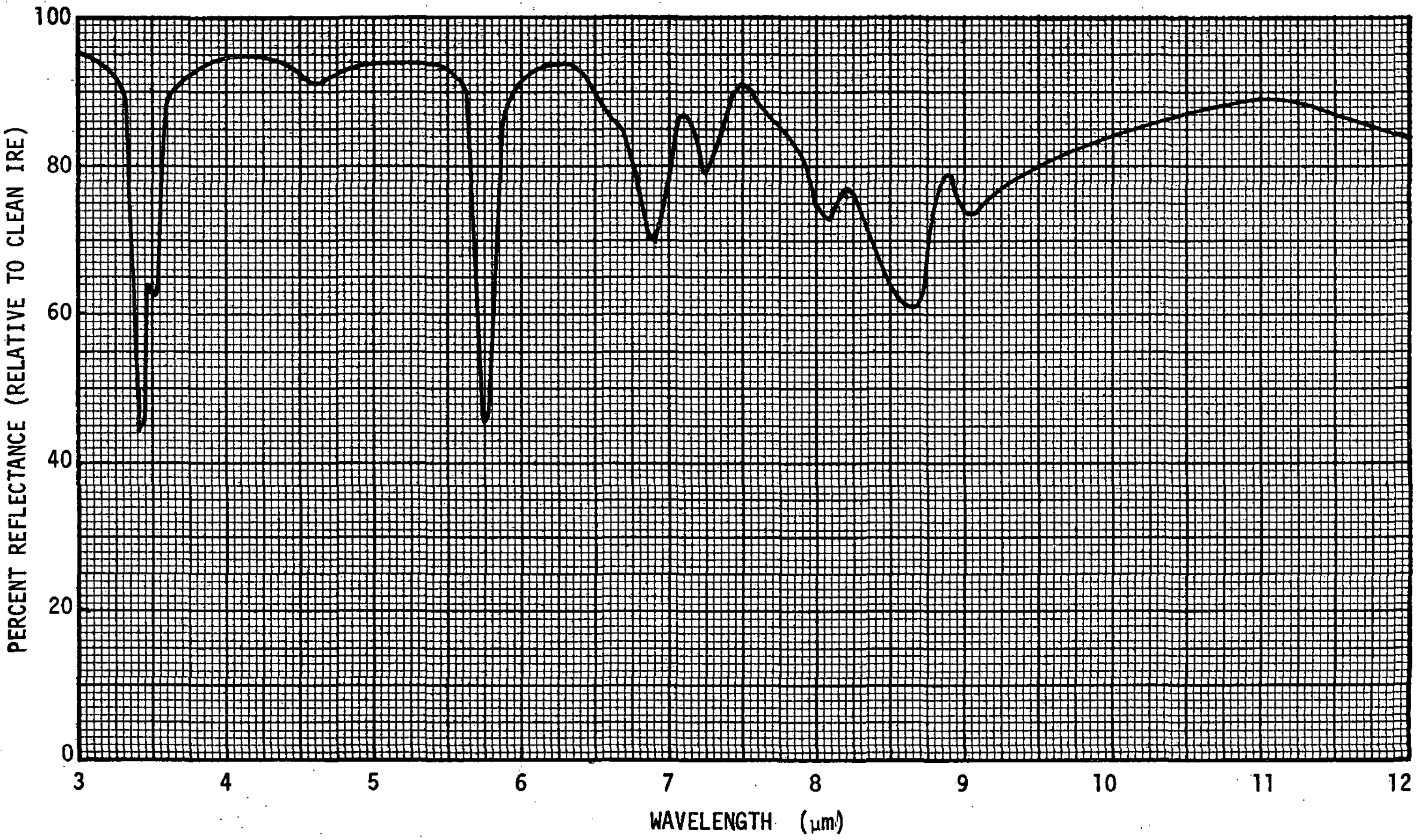

FIGURE 12. 3M BLACK VELVET COATING 401-C10 (COMPONENT I) ON 35-DEGREE GERMANIUM IRE

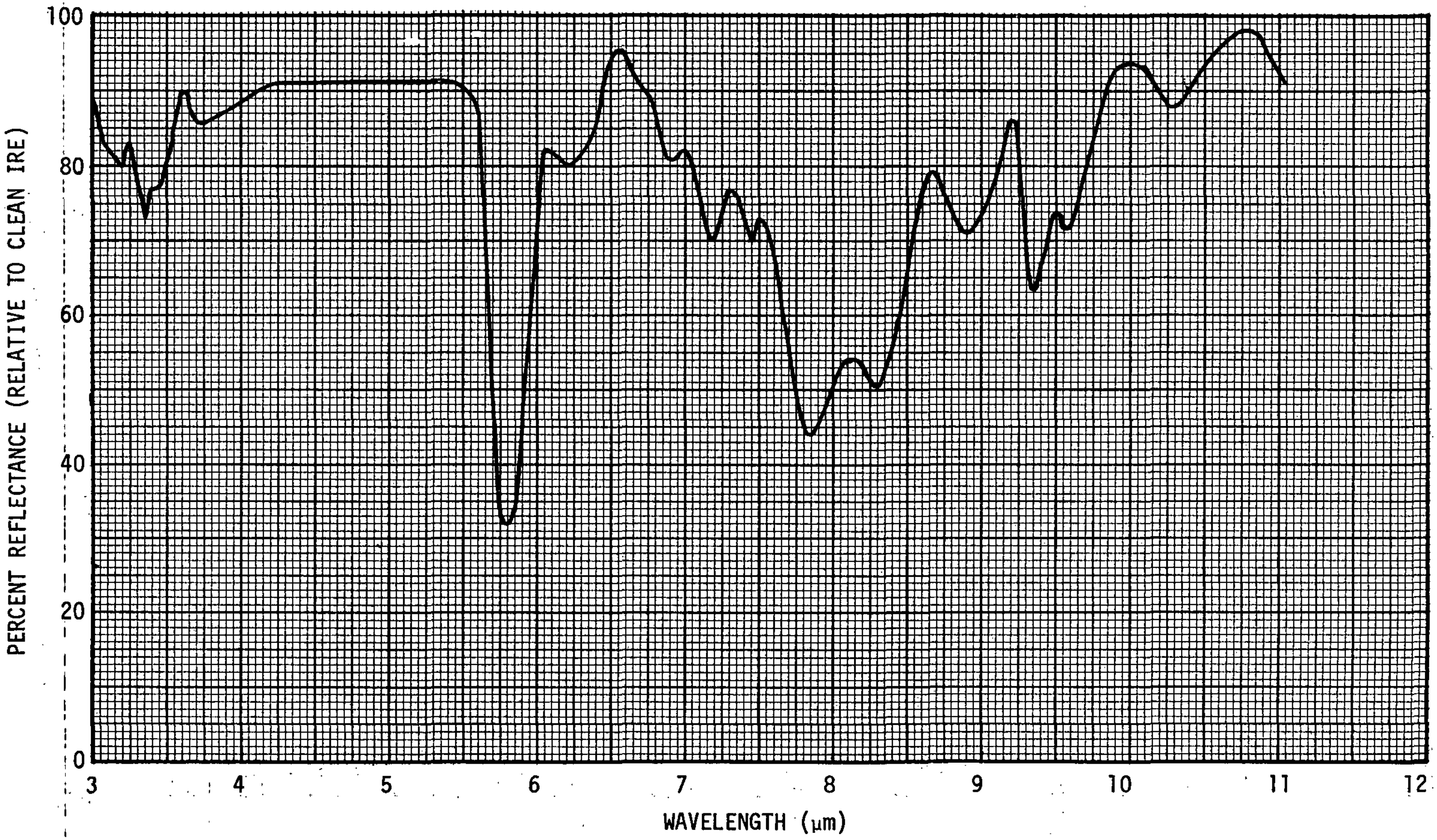

FIGURE 13. 3M BLACK VELVET COATING 401 SERIES (COMPONENT II) ON 35-DEGREE GERMANIUM IRE

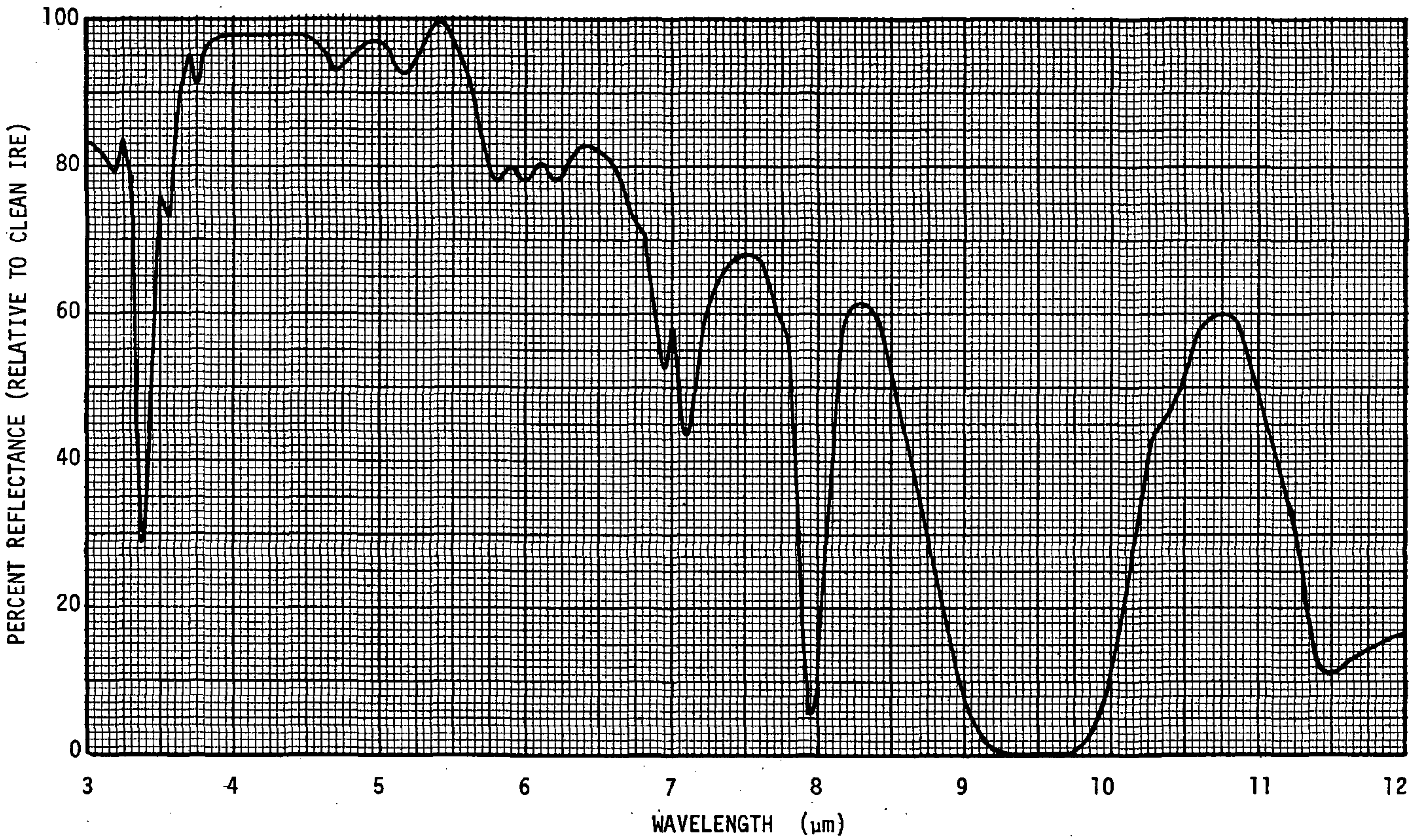

FIGURE 14. DC-11 ON 30-DEGREE KRS-5 IRE

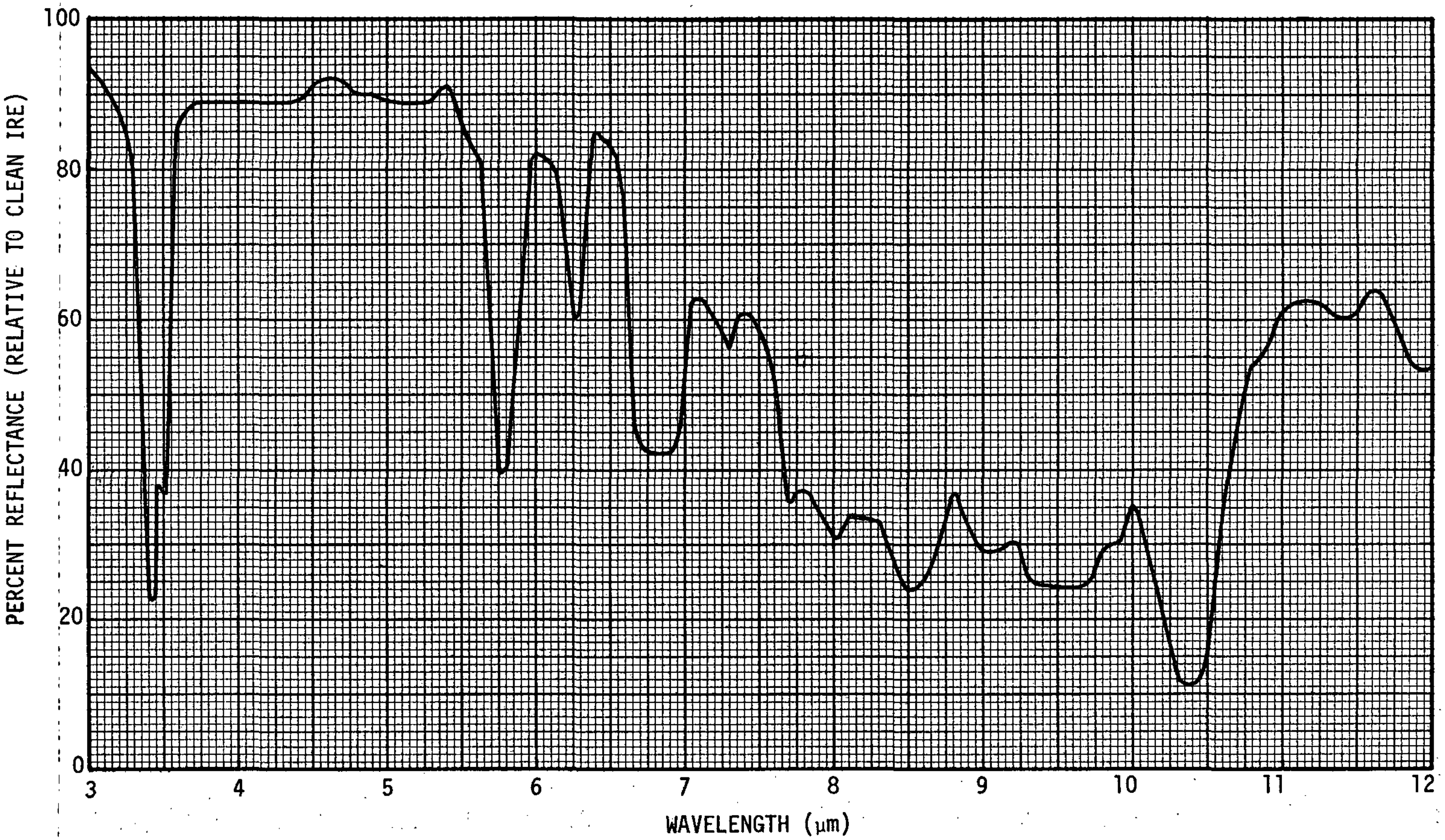

FIGURE 15. MIXTURE OF SUN VIS 706, HOUGHTO SAF 1120, DC-705, AND 3M BLACK VELVET ON 45-DEGREE KRS-5 IRE

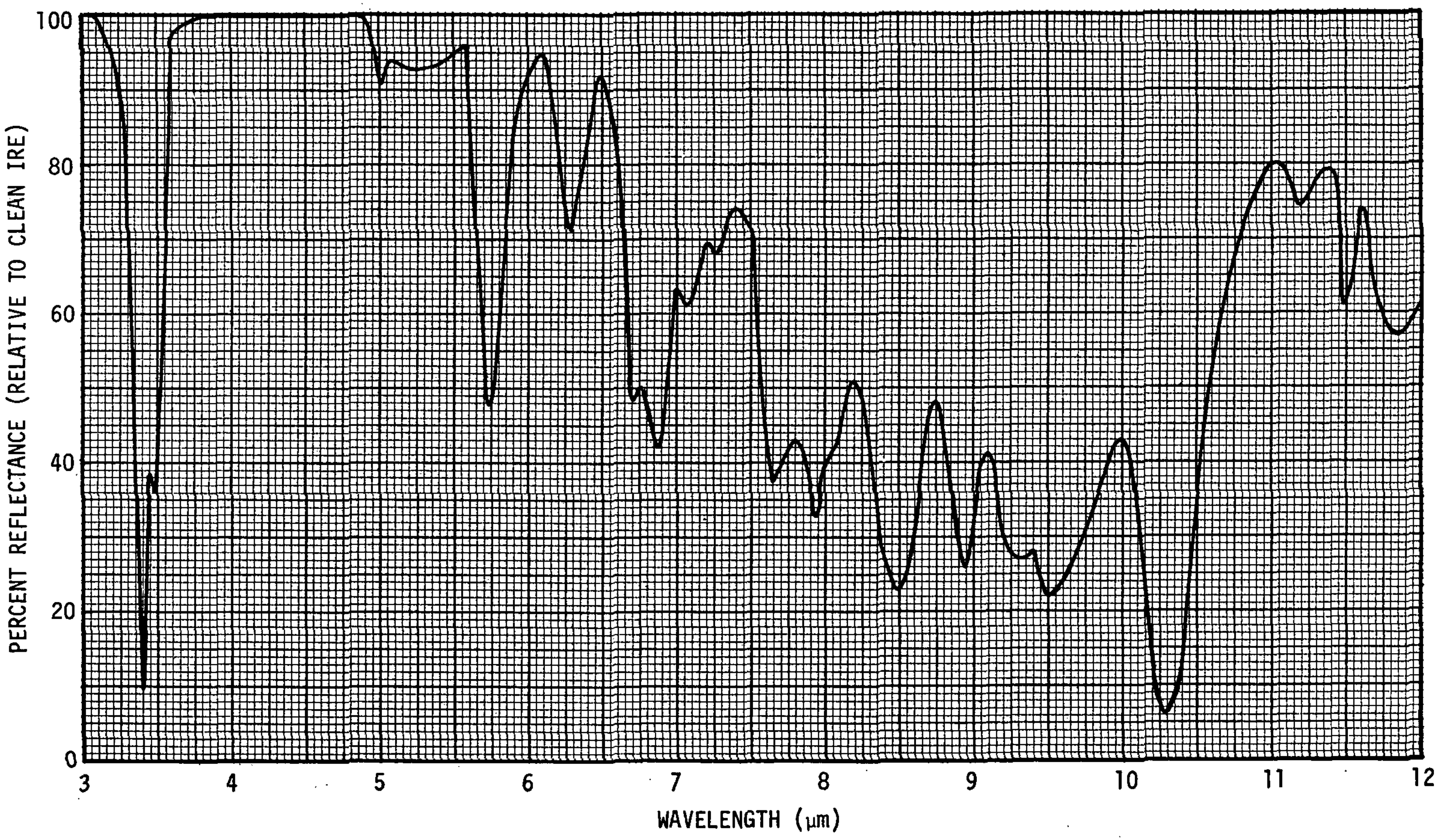

FIGURE 16. MIXTURE OF SUN VIS 706, HOUGHTO SAF 1120, DC-705, AND 3M BLACK VELVET ON 30-DEGREE KRS-5 IRE

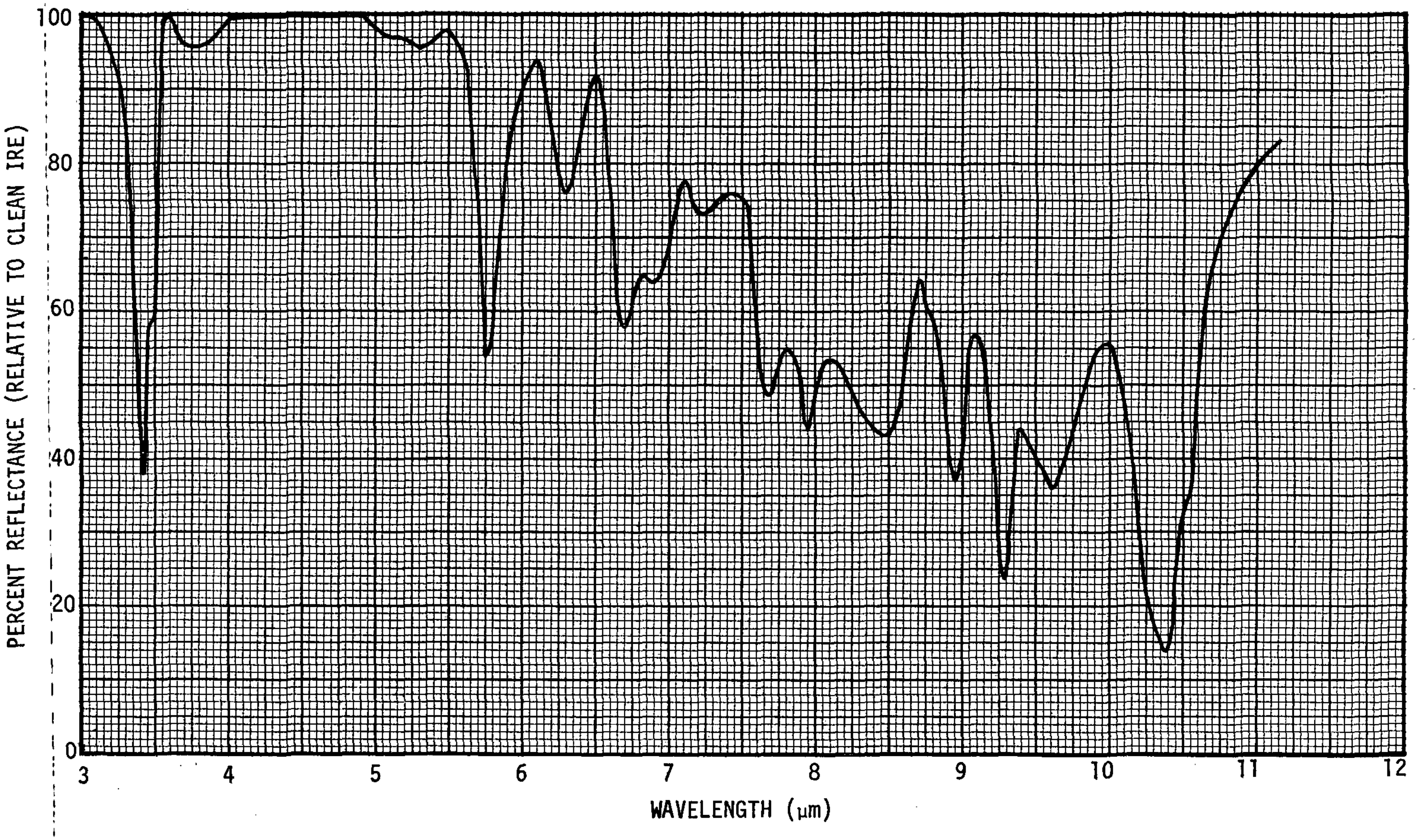

FIGURE 17. MIXTURE OF 3M BLACK VELVET, SUN VIS 706, DC-705, AND HOUGHTO SAF 1120 ON 35-DEGREE GERMANIUM IRE

4. THICKNESS EFFECTS ON SPECTRA

Spectra of DC-704 and Sun vis 706 were recorded for three different film thicknesses and are shown in Figures 18 through 21. The thinnest films shown are approximately 220 Å thick while the thickest films are approximately 2 micrometers thick. Spectra were also recorded for some films approximately 20 Å thick. However, the latter spectra are not very clean due to a high level of noise in the detector. These spectra will be discussed later.

Figure 18 shows spectra of three films of DC-704 on the 30-degree KRS-5 IRE. As can be seen, both the 175 Å film and the 1750 Å film are quite adequate for identification, with little or no spectral distortion. However, the 1.75-micrometer film shows almost total absorption for wavelengths greater than 7 micrometers and thus would not be useful for spectral identification. It should be borne in mind, however, that the 30-degree KRS-5 IRE was designed for thin films primarily and this effect was anticipated. The 35-degree germanium IRE, on the other hand, was designed for thick films as well as for thin films. Figure 19 shows DC-704 spectra on the 35-degree germanium IRE. Note that the 35-degree germanium IRE is not quite as sensitive as the 30-degree KRS-5 IRE (compare the 240 Å curve with the 175 Å curve on KRS-5) but that the spectra for the thick film (2.4 micrometers) is still very clean and undistorted for the 35-degree germanium IRE.

The same type behavior is demonstrated for Sun vis 706. Figure 20 shows Sun vis 706 on the 30-degree KRS-5 IRE and Figure 21 shows Sun vis 706 on the 35-degree germanium IRE. Again the 30-degree KRS-5 IRE shows distortion for the thickest film while the 35-degree germanium IRE exhibits no spectral distortion.

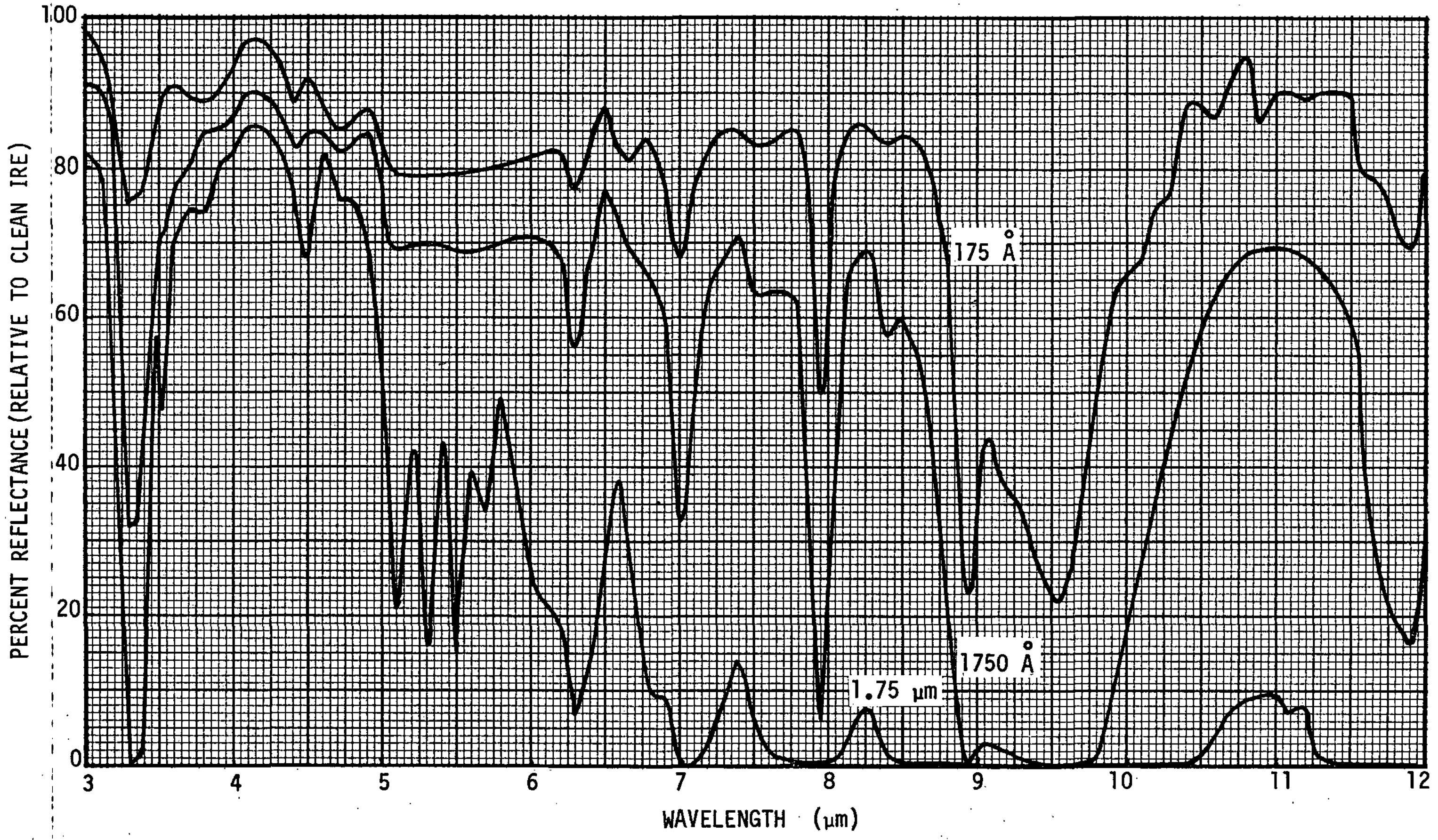

FIGURE 18. THREE FILMS OF DC-704 ON 30-DEGREE KRS-5 IRE

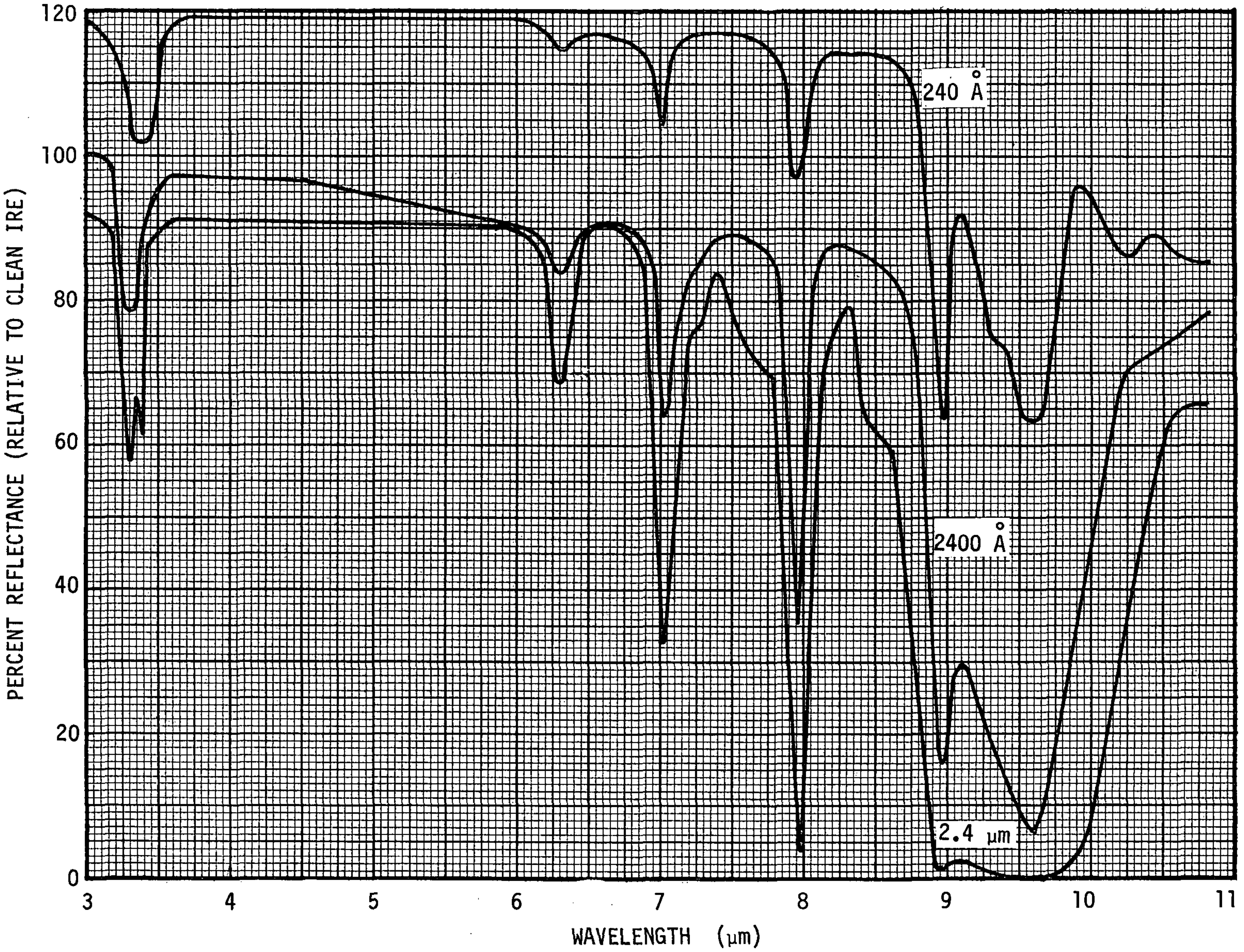

FIGURE 19. THREE FILMS OF DC-704 ON 35-DEGREE GERMANIUM IRE

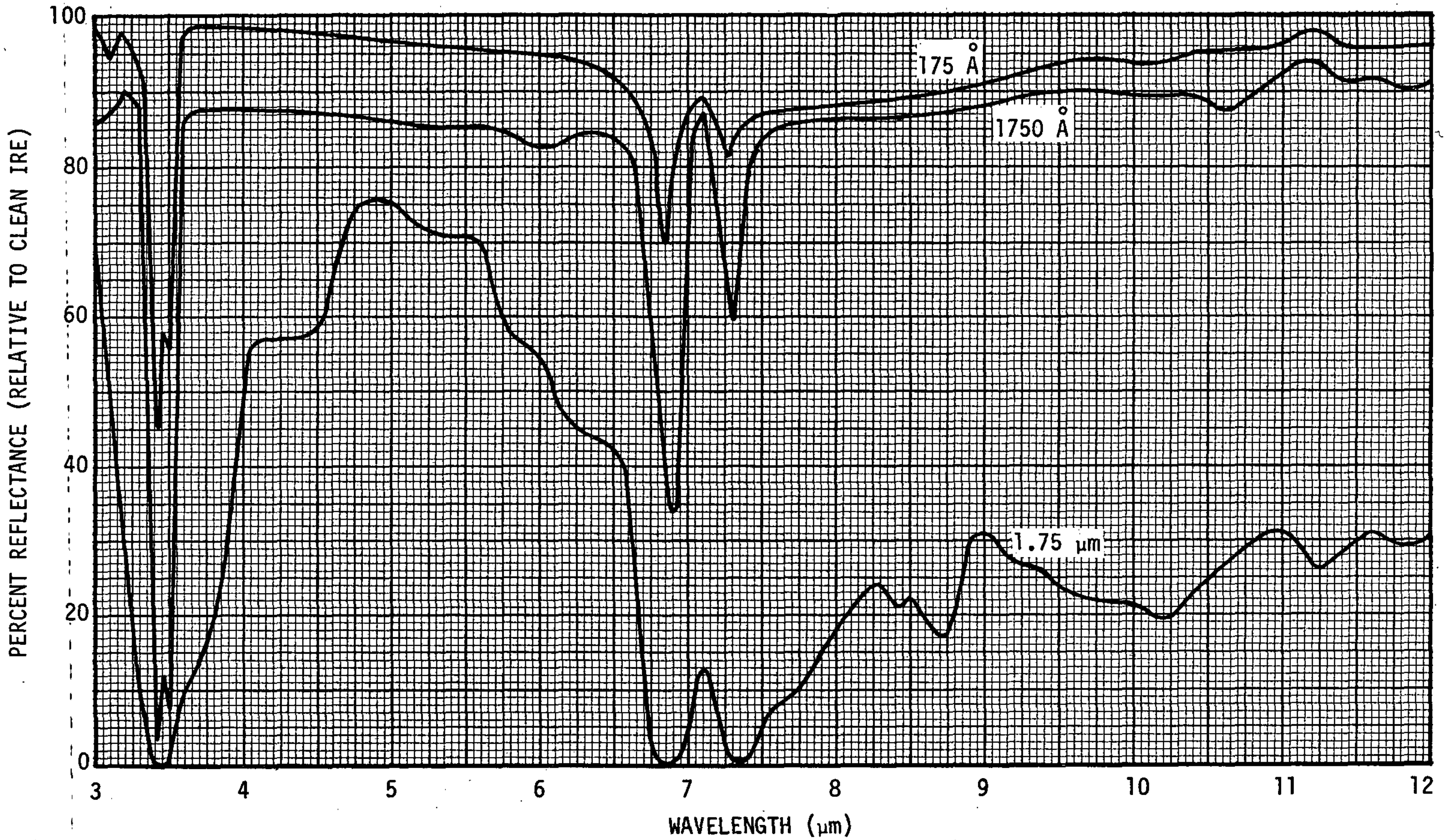

FIGURE 20. THREE FILMS OF SUN VIS 706 ON 30-DEGREE KRS-5 IRE

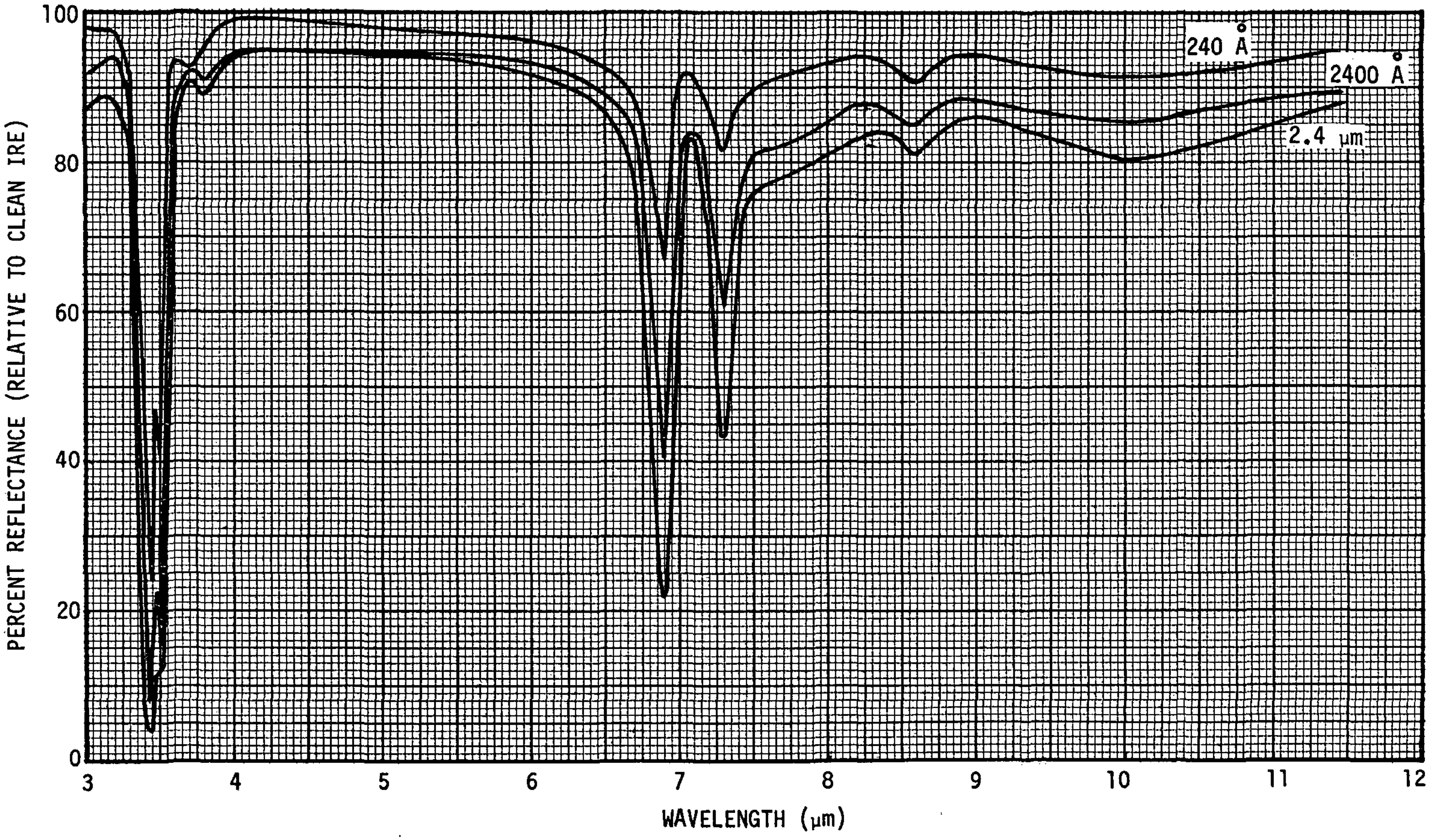

FIGURE 21. THREE FILMS OF SUN VIS 706 ON 35-DEGREE GERMANIUM IRE

5. MINIMUM DETECTABLE FILM THICKNESS

A primary effort of the Phase I study was to develop a technique for detecting and identifying contaminant films only a few monolayers in thickness in real time. Two IRE configurations were suggested for this purpose -- the 30-degree KRS-5 IRE and a 40-degree germanium IRE used in conjunction with a KRS-5 backing as the third medium. Calculations indicate that the germanium/KRS-5 combination should be approximately ten times as sensitive as the 30-degree KRS-5 IRE.

From a practical standpoint, it now appears that the germanium/KRS-5 arrangement is too difficult to employ as a routine contaminant monitoring technique. Figure 22 shows spectra of the 3.4-micrometer band of Sun vis 706 for a 20 Å film on the 40-degree germanium/KRS-5 IRE. Although the germanium/KRS-5 combination is somewhat more sensitive, it is not ten times as sensitive. The most probable explanation for this is that the KRS-5 backing is not making good optical contact with the germanium. This lack of sufficient contact is probably due to nonuniformity of the contaminant deposit and to variations in the KRS-5 surface flatness. The KRS-5 backing plate was finished as flat as conventional technology permits. However, KRS-5 is extremely soft and cannot be finished as flat as germanium. Also, KRS-5 is somewhat plastic and cold flows readily. For these reasons it appears that practical use of the germanium/KRS-5 combination would not be a significant improvement over the use of the 30-degree KRS-5 IRE.

Consequently, spectra of films approximately 20 Å thick of several of the contaminants of interest were measured using the 30-degree KRS-5 IRE. Because of the high level of noise in our particular detector, it was necessary to integrate the signal over a relatively long

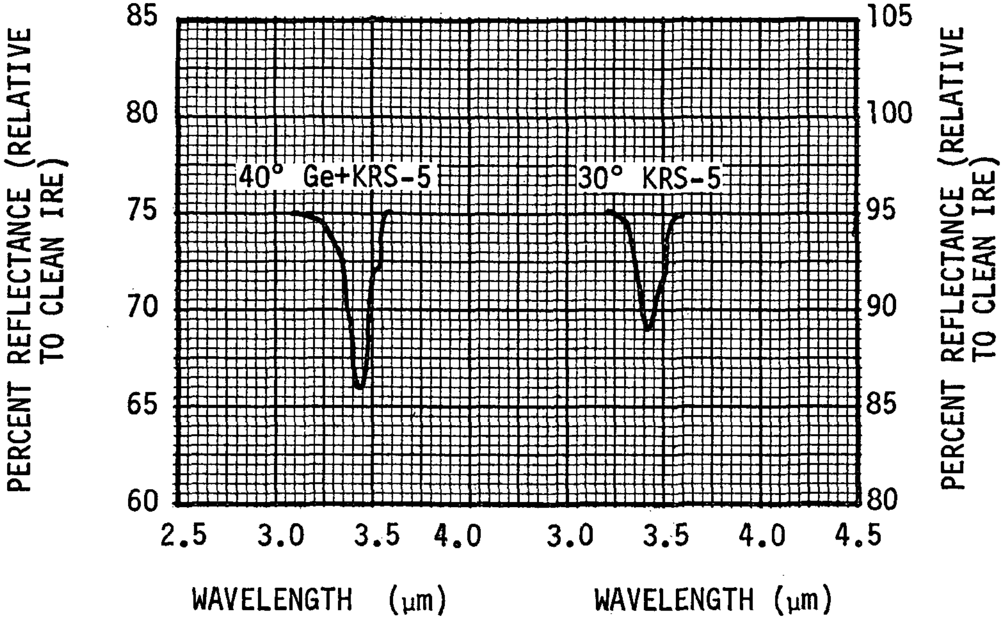

FIGURE 22. SPECTRA OF 3.4-MICROMETER BAND OF SUN VIS 706 FOR FILM APPROXIMATELY 20 Å THICK

time period (we used a 3-second time constant) and the scan therefore had to be made very slowly. Consequently, only one material (3M Black Velvet component I) was scanned completely at this rate. Selected bands of the other contaminants were scanned rather than complete spectra.

Figure 23 shows the spectra of a 20 Å film of 3M component I on the 30-degree KRS-5 IRE. Note that the reflectance exceeds 100 percent much of the time. We found this to be the case for all of the very thin films on KRS-5 and for some of the 200 Å films on KRS-5 and on germanium. The change in reflectance at the stronger bands for the 3M component I was 12 percent for the 3.4-micrometer band and 12 percent for the 5.8-micrometer band. The thickness which would produce a ten percent change at the 5.8-micrometer band was calculated to be 29 Å during the Phase I study, assuming a film refractive index of 1.5 (see Table 6, Volume I). The experimental results agree quite well with the theoretical predictions.

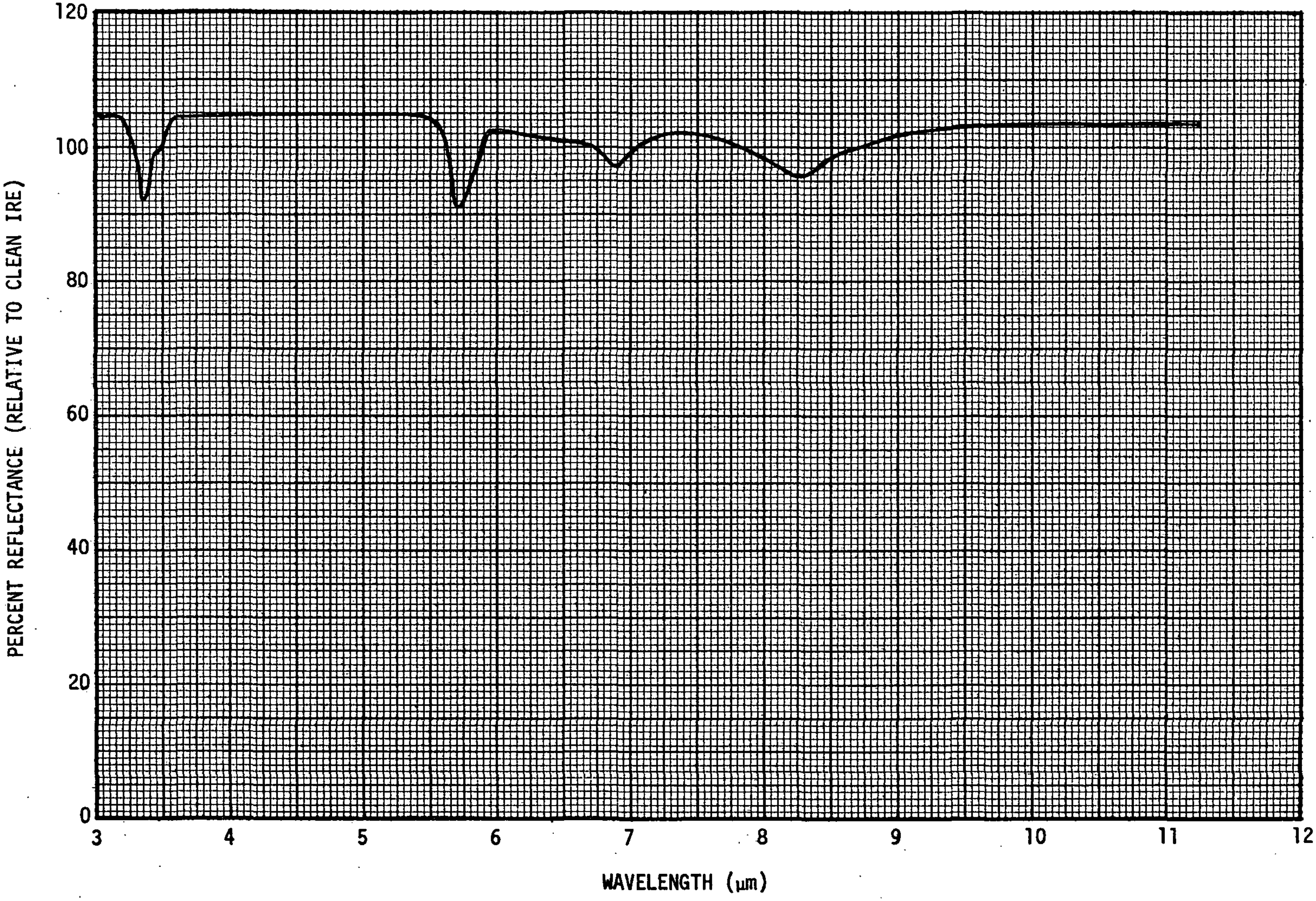

FIGURE 23. 20 Å FILM OF 3M BLACK VELVET COATING COMPONENT I ON 30-DEGREE KRS-5 IRE

Figure 24 shows a similar scan of three bands of 20 Å thick DC-705 (note the expanded wavelength scale). The 7-micrometer band shows a 5 percent change, the 8-micrometer band shows a 7 percent change, and the 9.5-micrometer band shows a 12 to 15 percent change in reflectance. These results also agree well with the predictions of the Phase I study.

The results of these studies indicate that spectra of the contaminants of interest can be obtained from film approximately 20 Å thick and used to identify the contaminants providing the monochromator-detector system is efficient. The primary difficulties encountered in this specific study effort were due to the low signal-to-noise ratio of our optical system rather than to the sensitivity of the IRE.

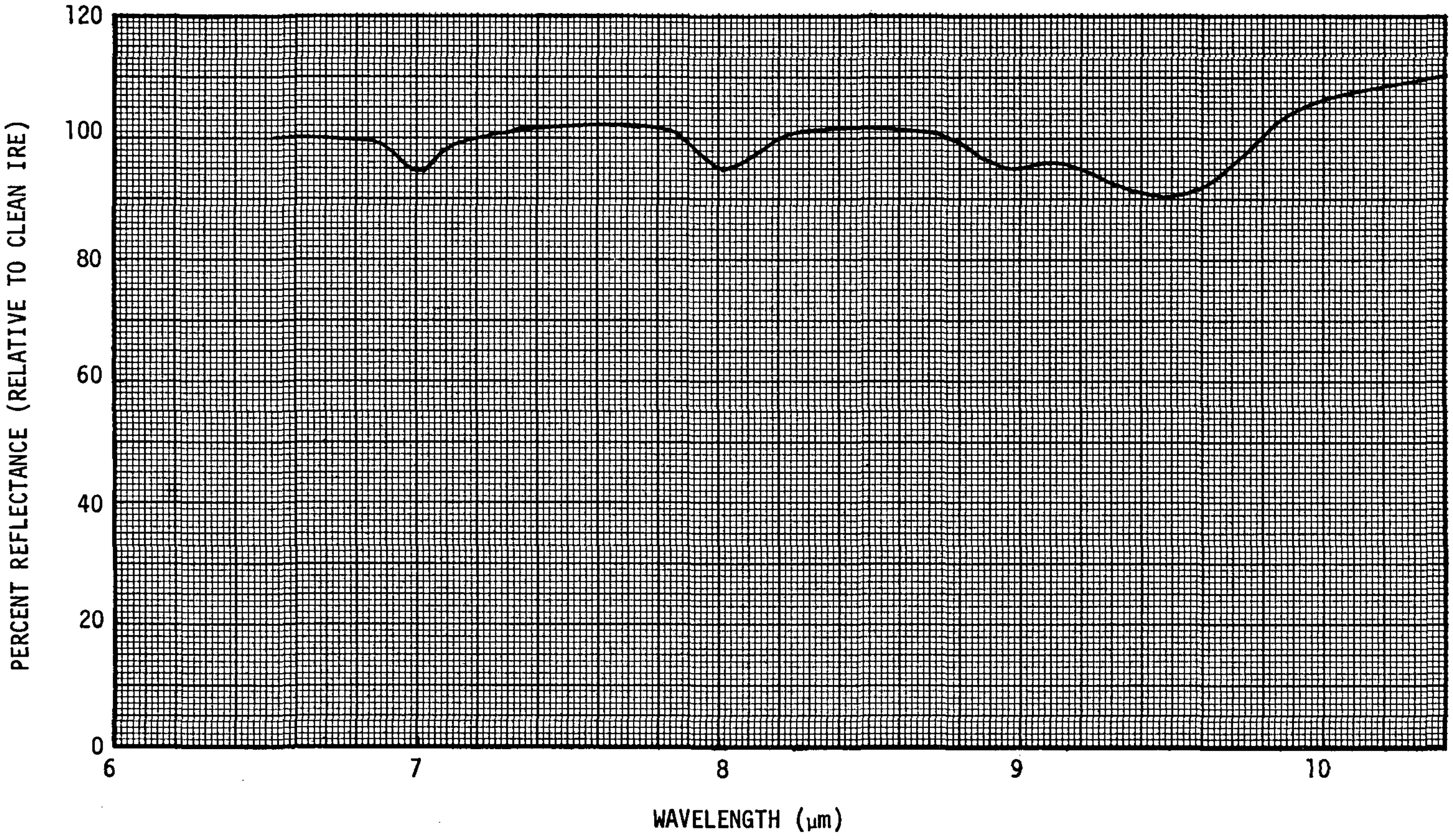

FIGURE 24. 20 Å FILM OF DC-705 ON 30-DEGREE KRS-5 IRE

6. CONCLUSIONS

The Phase II work has experimentally verified the analytical results of the Phase I study and has demonstrated the feasibility of using ATR techniques to detect and identify contaminant deposits. This work has shown that it is possible to identify contaminants with deposits as thin as 20 Å from infrared ATR spectra obtained with a 30 degree, 46 reflection KRS-5 element using radiation polarized parallel to the plane of incidence. It has also demonstrated that thick film or bulk spectra can be obtained undistorted by using a 35-degree, 26 reflection germanium element.

The quantitative analysis of a complex spectrum of a multicomponent mixture yielded the concentrations of the individual components with an accuracy of ±50 percent for the worst masked bands and ±10 percent for the most easily interpretable bands. This example demonstrates the feasibility of quantitative multicomponent mixture analysis. Had the Houghto-Saf 1120, a material with very strong bands across the entire spectral range, been omitted from the mixture, an overall accuracy of ±10 percent could probably have been obtained.

The proposed 40-degree germanium/KRS-5 combination did not perform as well as anticipated, due primarily to the difficulty of maintaining optical contact between the germanium and the KRS-5 with a contaminant present. Also, the KRS-5 is extremely soft and deforms easily so that maintaining the uniform optical contact necessary is impractical.

The 35-degree, 26 reflection germanium element showed high sensitivity with thin films (although not as high as that of the 30-degree

KRS-5) and displayed no spectral distortion with thick films or bulk spectra. In addition, the germanium is easily cleaned and is very hard, making it ideal for use in all applications except those demanding the highest sensitivity.

7. RECOMMENDATIONS

Based on the results of this work, the use of infrared ATR techniques to monitor and identify contaminant deposits is recommended whenever real-time analysis is desired.

The design and development of an ATR instrument capable of operating completely within a space simulation chamber, with provisions for external readout, is recommended as the next logical project in the development of the real-time contaminant identification monitor. However, prior to instrument development, IREs could be placed within the chamber before a test, left in the chamber during testing and measured after cessation of the test to determine contaminant deposition after the fact.

An ATR instrument for real-time contamination analysis should be designed to use both a 30-degree, 46 reflection IRE and a 35-degree, 26 reflection IRE in order to be able to obtain interpretable spectra of both very thin and very thick films. The instrument should cover the spectral region from 2.5 to 15 micrometers and should have a resolution of at least 0.03 micrometer. The incident radiation should be polarized with the electric field vector parallel to the plane of incidence at the totally reflecting interface and the angle of convergence of the incident beam should not exceed a 5-degree half angle.

To avoid rapid intensity fluctuations in the incident energy, it would be desirable to use a filter wheel monochromator rather than a grating instrument. However, the resolution requirements may pose a problem with this selection. The detector and electronics should be such as to provide a signal-to-noise ratio sufficient to detect a change in reflectance of approximately one percent. With the low energy sources in use in the infrared, a low impedance detector (2 to 100 ohms) is probably best suited for this application.

If automated readout and storage is desired, the data can be digitized and stored on paper or magnetic tape, and the instrument can be designed to scan through the wavelength interval at selected time intervals.

If standard manual operation is desired, all that is required is electrical feedthroughs for power to operate the drive mechanisms and to transmit the analog output to a strip chart recorder.