

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP017699

TITLE: Application of Mid-Infrared Spectroscopy to the Identification of Materials and to the Determination of Surface Coatings

DISTRIBUTION: Approved for public release, distribution unlimited  
Availability: Document partially illegible.

This paper is part of the following report:

TITLE: Proceedings of the Tri-Service Environmental Technology Workshop, "Enhancing Readiness Through Environmental Quality Technology" Held in Hershey, PA on 20-22 May 1996

To order the complete compilation report, use: ADA429790

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:  
ADP017697 thru ADP017729

UNCLASSIFIED

# APPLICATION OF MID-INFRARED SPECTROSCOPY TO THE IDENTIFICATION OF MATERIALS AND TO THE DETERMINATION OF SURFACE COATINGS

G. Louis Powell  
Oak Ridge Y-12 Plant<sup>a</sup>, Lockheed Martin Energy Systems, Inc.  
Oak Ridge, Tennessee 37831-8096  
(423)574-1717  
(423)574-2582  
plg@ornl.gov

Edward G. Engbert  
U.S. Army Environmental Center  
APG, MD 21010-5401

James Holiday and Jose L. Velez  
Corpus Christi Army Depot  
Corpus Christi, Texas 78419-6000

## ABSTRACT

A small user friendly, light-weight, field hardened, computer controlled device for performing infrared spectroscopic analysis, with high sensitivity of trace contamination on surfaces, has recently been defined by Lockheed Martin Energy Systems, Inc. The National Aeronautics and Space Administration at Marshall Space Flight Center, Alabama (NASA/MSFC) initiated a development contract to field a production model of this device with Surface Optics Corporation, San Diego, California in order to certify the sandblasted inner surface of solid rocket motor casings to be free of both hydrocarbon grease and silicone oils at levels approaching 1 milligram per square foot. Through contracts with Lockheed Martin Energy Systems, Inc., the Army acquired a prototype of this instrument, which was used for optimizing the performance with respect to detecting trace organic contamination on sandblasted metal surfaces. That prototype has since been upgraded to incorporate the refinements discovered in its use, and is presently being field tested by the Army at the Corpus Christi Army Depot (CCAD). Referred to as a surface inspection machine-infrared (SIMIR or SOC 400), this device employs a miniature Fourier transform Infrared spectrometer (FTIRS) with very efficient diffuse reflectance optics to provide reflectance spectra of surfaces measured relative to some reference surface. These spectra are capable of yielding qualitative and quantitative chemical information from a host of surfaces that has imminently practical applications in the determination of surface identification, contamination, and degradation. The performance of the SIMIR and its initial applications to surface inspection at CCAD that include sandblasted metal surfaces, as well as, detection of contamination on other metal finishes such as black oxide finished steel.

## 1. INTRODUCTION

Alternative industrial cleaning processes are increasingly being implemented throughout the Department of Defense due to the environmental banning of halogenated cleaning solvents. However, the uncertainty associated with the effectiveness of the new cleaning processes often requires that the level of cleaning be verified prior to the continuation of manufacturing processes such as painting or surface plating. Many of

---

<sup>a</sup>Managed for the U. S. Department of Energy by Lockheed Martin Energy Systems, Inc. Under Contract No. DE-AC05-84OR21400

these tests are time consuming, do not provide definitive results, and will not quantify levels of cleanliness to a high level of accuracy.

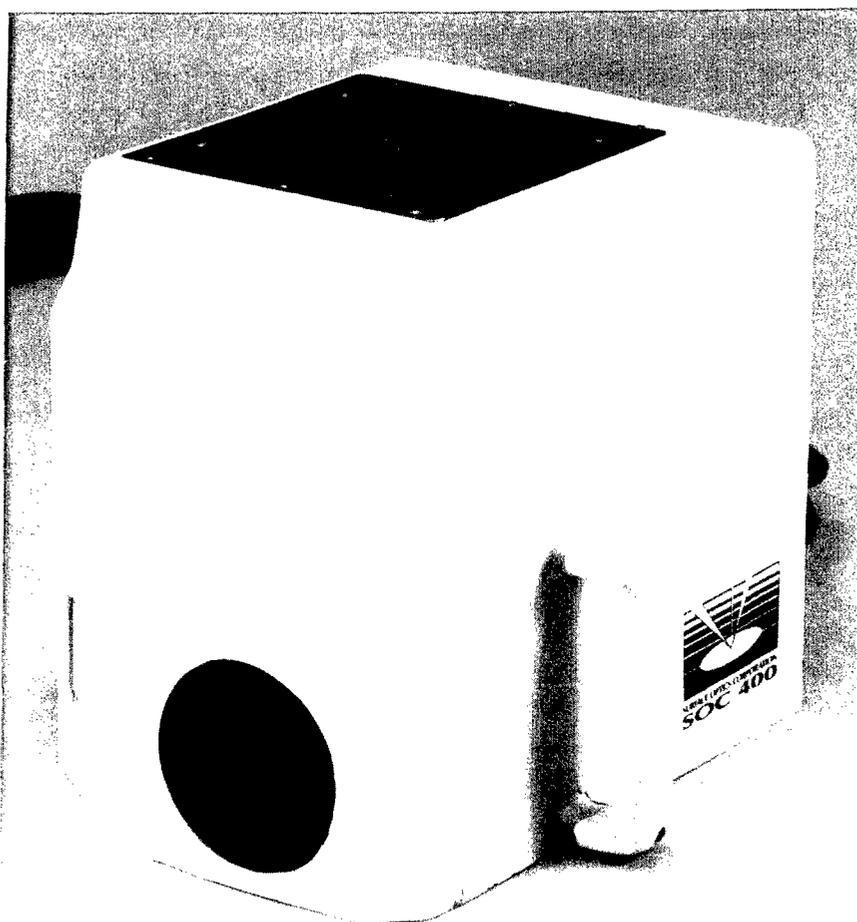
Diffuse reflectance mid-infrared spectroscopy is a very useful tool for the inspection of surfaces in manufacturing applications,<sup>1</sup> particularly those related to the cleaning of metals. In collaboration with Harrick Scientific Corporation, remote sensing infrared accessories have been developed and field demonstrated to be practical means of surface inspection for organic contamination on metals<sup>2,3</sup>, lithium hydroxide on lithium hydride<sup>4</sup>, and heat damage to graphite-epoxy laminates<sup>5</sup>. The method is also applicable to identifying organic solids; and for characterizing textiles, paper, wood, coal, and adhesives<sup>1,6</sup>. Recent collaboration between the Lockheed Martin Energy Systems, Inc., NASA/MSFC, the Army, and Surface Optics Corporation has extended these developments to the extent that practical, user-friendly, very-sensitive infrared surface inspection machines are in service at sites of these collaborators, and are available in the market place<sup>6</sup>.

The Surface Optics Corporation SOC 400 Surface Inspection Machine / InfraRed (SIMIR)<sup>6</sup> was designed to meet a NASA requirement that the sandblasted inner surface of solid rocket motor casings be free of both hydrocarbon grease and silicone oils at levels approaching 1 milligram per square foot (~ 10 nm films). Through contracts with Lockheed Martin Energy Systems, Inc., the Army acquired a prototype of this instrument, which was used for optimizing the performance with respect to detecting trace organic contamination on sandblasted metal surfaces. That instrument has since been upgraded to incorporate the refinements discovered in its early use. This SOC 400 is presently being field tested by the Army at the Corpus Christi Army Depot (CCAD), where infrared surface inspection is being extended to surfaces that are more challenging than sandblasted metals. This paper describes this hand-held (or remotely positioned) Fourier transform infrared spectrometer (FTIRS) that uses diffuse reflectance optics to interrogate surfaces. The performance is demonstrated in terms of the signal-to-noise of the instrument (i.e., the sensitivity of the SOC 400 in spectrometric units) when used to inspect highly reflective sandblasted surfaces, the fingerprints of contaminants (various oils and soap residues) on metals at approximately the 100 mg per square foot level, and to the inspection of machined, black oxide finished steel gear components where the analysis is complicated by the lower light scattering ability of machined surfaces and the presence of spectral features due to the black oxide film.

## 2. THE SOC 400 SIMIR

The Surface Optics Corporation SOC 400 Surface Inspection Machine / InfraRed (SIMIR)<sup>6</sup> shown in Figure 1 weighs less than 8 Kg and may be operated at any orientation. The SIMIR is based on barrel ellipse diffuse reflectance optics having a focal point located in the plane of an opening in the face plate of the instrument. This barrel ellipse optical configuration is shown in Figure 2. The system is supported by either 12 VDC or 120 VAC and a computer using MIDAC GRAMS/386. At this workshop, the SOC 400 was operated from a 90 MHz Pentium Computer and, interchangeably, with a 486 laptop computer. The SOC 400 operates at <40 W, slightly less than the power requirements for the laptop computer. This "point-and-shoot" type of instrument allows rapid in-field analyses to be made with sensitivity comparable to laboratory FTIRS. Dedicated scanning and collection routines, and the robust characteristics of the barrel ellipse focal point with respect to sample positioning substantially enhance the utility of the SOC 400. The capability for having the spectrometer software instruct positioning devices in a noncontact mode is sometimes utilized<sup>3,6</sup>, usually with dramatic increases in productivity and utility.

The key to the performance of the SIMIR is the integration of an intense source, very efficient collection of diffusely scattered light, and an infrared light detector having very high signal-to-noise, the achievement of which, for a given collection time interval is the best method for defining performance in a FTIRS. That

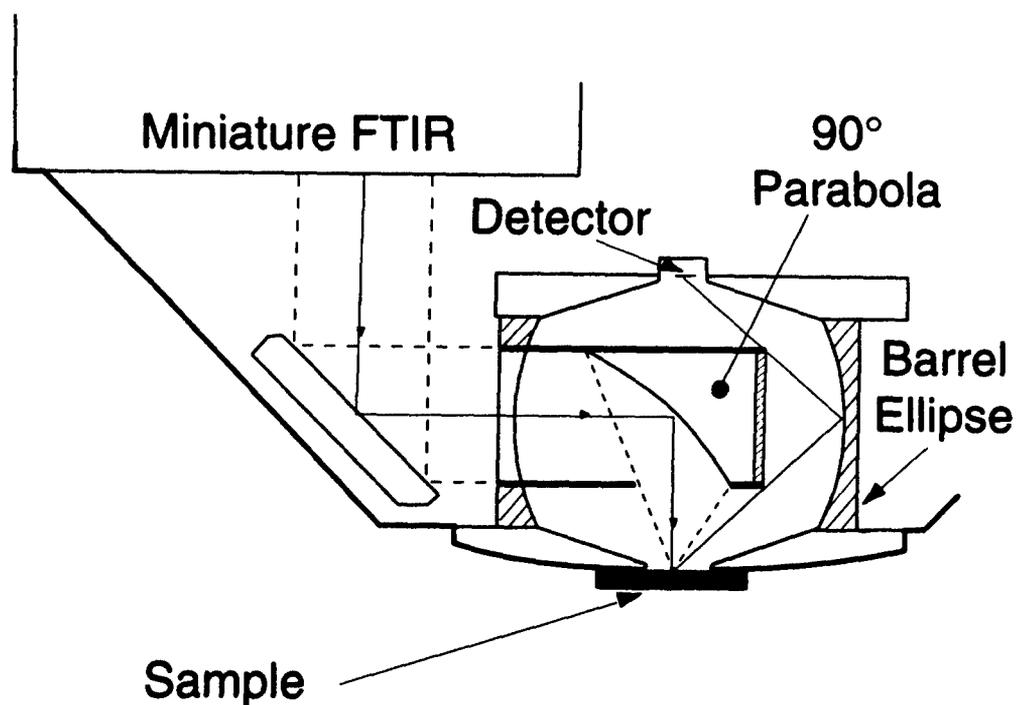


**Figure 1. The SOC 400 Surface Inspection Machine/InfraRed (SIMIR). The sampling point of the diffuse reflectance optics is at the center of the 85-mm diameter dark circle.**

function is described in Figure 3. The operating system may also be customized using MIDAC/Grams386/Array Basic or MIDAC Visual Basic software for dedicated inspection operations. This is done to make the inspection operation user friendly, hardened against accidental loss of data and changes in operational parameters, to introduce dedicated post processing of data, and to instruct external devices by serial communications to reposition the specimen and execute other operations.

### 3. SURFACE INSPECTION OF METALS

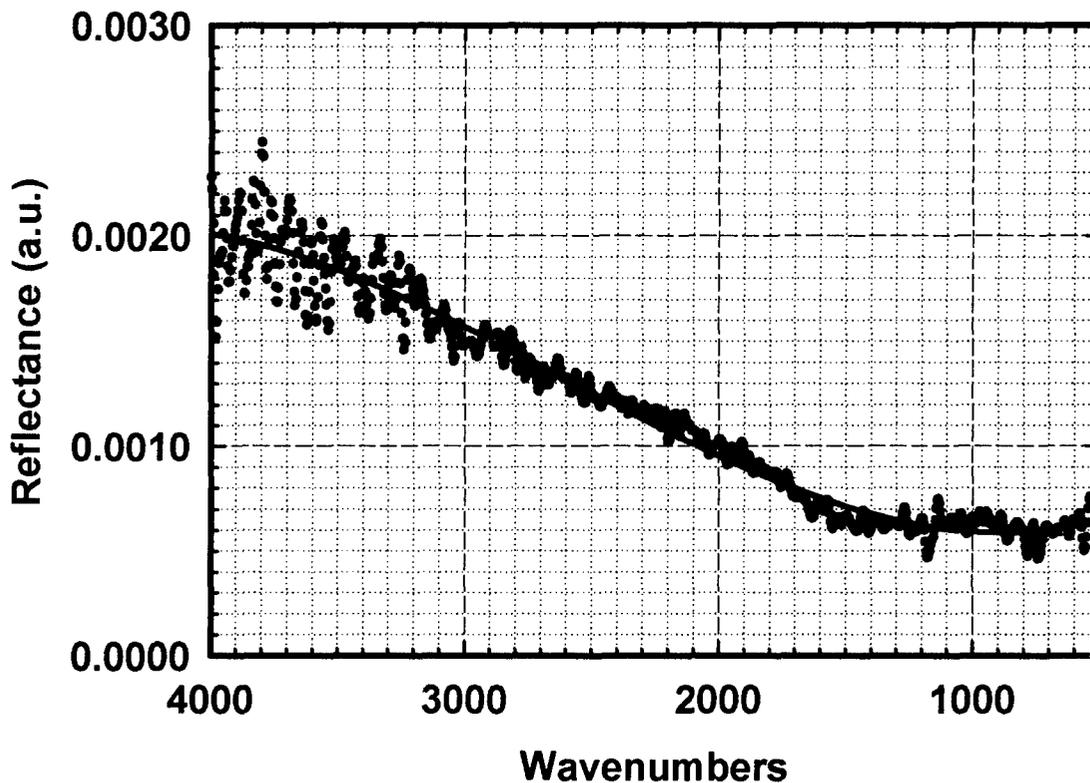
The SOC 400 operates in a similar fashion to most laboratory FTIRS, a characteristic that makes its operation and data evaluation very familiar to most experimental chemists. The difference with respect to laboratory instruments is that aligning accessories and waiting for the spectrometer to purge no longer exist. The SOC 400 and the specimen surface are brought into appropriate proximity, made easy by the contact face plate, and the spectrum is collected while observing the spectrum develop in nearly real time (1.3 s phase lag). With respect to observing stains on metals, a fortuitous property of sandblasted metals (the archtypical surface for adhesive bonding to metals) is that applying a nonvolatile oil or powder to sandblasted metal substrates, followed by vigorous scrubbing of the substrate with a simple tissue to remove as much residue as possible, leaves an optimum residue for producing a library spectrum.



**Figure 2. The barrel ellipse diffuse reflectance collection optics in the SOC 400. The collimated beam from the FTIRS is focused on the sample by a parabolic mirror. Light scattered by the sample at angles greater than the angles of incidence are focused on the detector by the barrel shaped elliptical mirror.**

Now that the acquisition of spectra has been greatly simplified, the focus turns to the hard part. An infrared spectrum is a measure of light absorption in one substrate relative to another, usually called the reference or background. With respect to certifying the cleanliness of metals, the inspector must know that the reference spectrum is clean within the detection limits of the method. Contamination must not be transferred from one substrate to another, an event that is easily avoided by operating in a noncontact mode. In the process of cleaning metals, this is the technique intensive process of keeping a clean part clean.

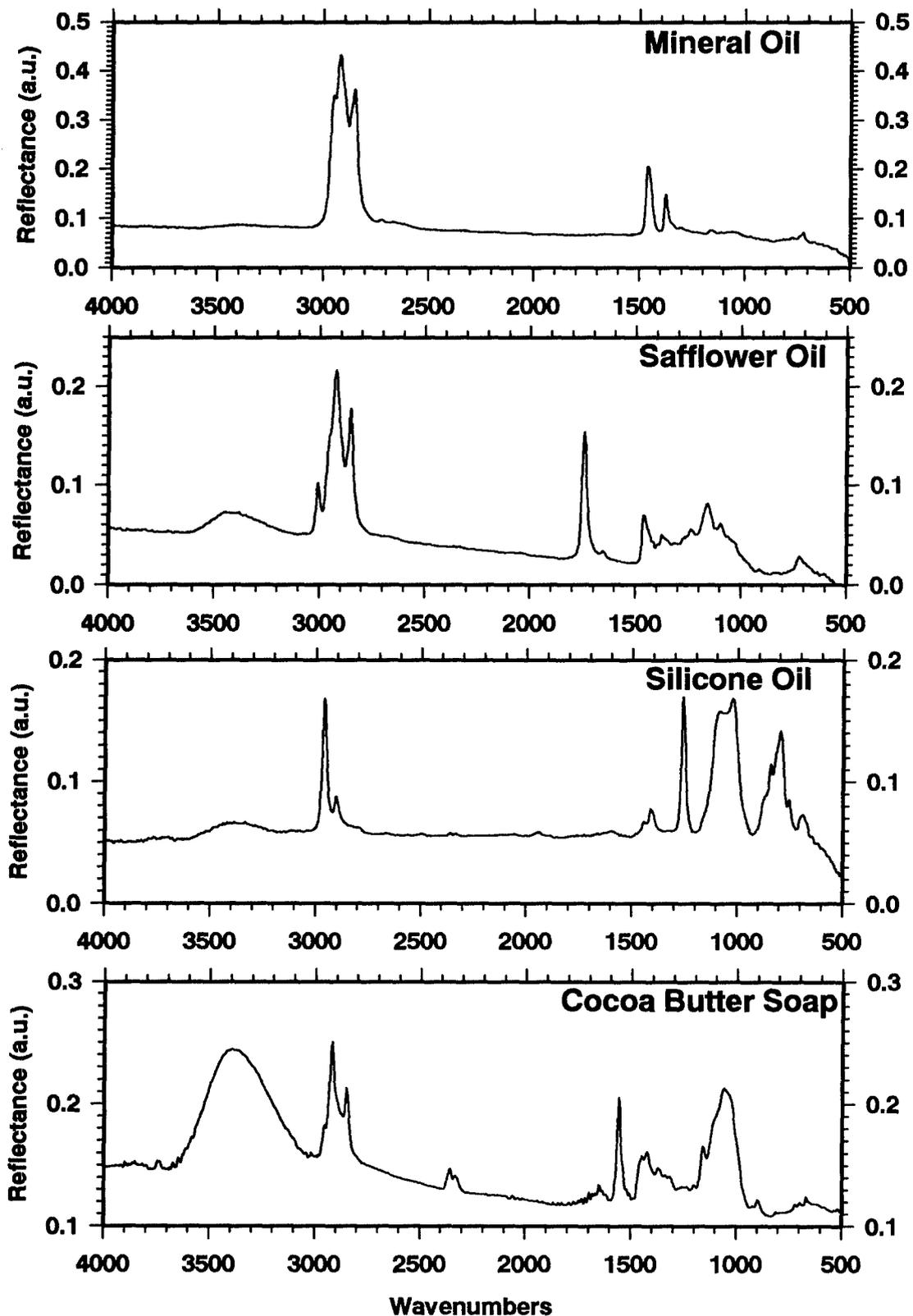
Sandblasted gold is the optimum substrate material for metal cleanliness studies because gold is easily cleaned. Gold it can be cleaned with very harsh chemical methods. Gold is one of the most reflective of metals and displays no features related to oxide films. Thus, sandblasted gold returns to the infrared detector a true representation of the spectral distribution of the incident beam. Sandblasted aluminum is also a good substrate, but the aluminum oxide film can significantly contribute to the spectral features. Highly anodized aluminum strongly absorbs over much of the mid infrared spectral range. Sandblasted stainless is also a good substrate in that it is very durable and cleanable. It does contribute some oxide film features to the spectra. Again the emphasis is on this form of surface inspection as a comparative technique suggesting that the background spectrum for surface cleanliness approximate as closely as possible the clean substrate of the surface being analyzed.



**Figure 3.** An infrared spectrum obtained from a sandblasted gold specimen using  $16\text{ cm}^{-1}$  resolution, 2 times zero filling, and 48 coadded scans (1 min.) referenced to the same specimen background spectrum collected for 256 coadded scans. The graph shows the noise in the spectrum relative to a fourth order polynomial curve fit to the data.

### 3.1 LIBRARY SPECTRA

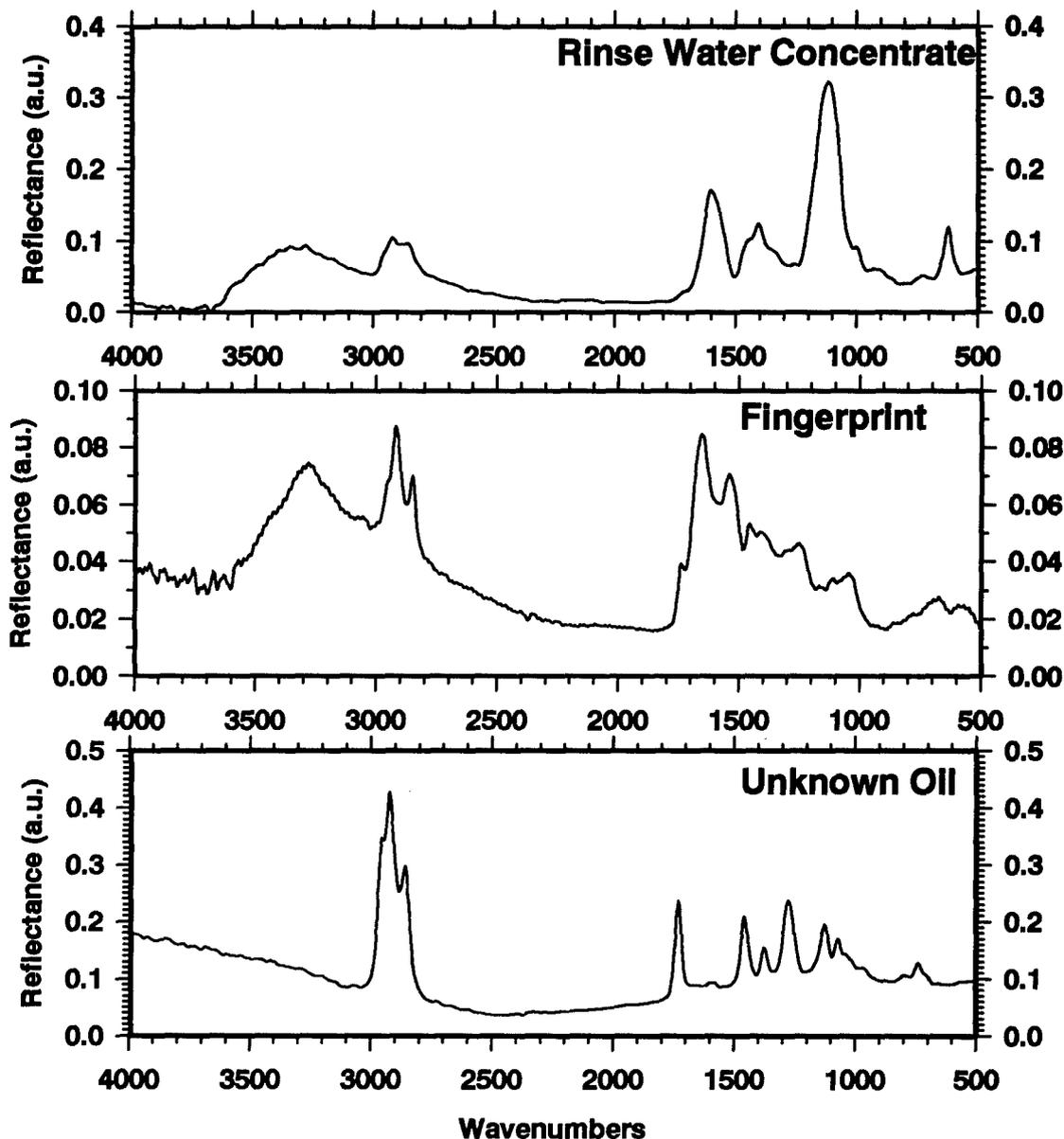
Figure 4 shows library-type spectra of common classes of contaminants found in cleaning operations. The mineral oil spectrum is pharmaceutical grade light mineral oil. The strongest band is due to the stretching frequencies of aliphatic hydrocarbons and is the general signature of contamination by organic materials. The remaining two weaker bands define the stain as a simple hydrocarbon. Many commercial greases and oils fit this pattern, but they may be complicated by additives that may uniquely identify the source of the contamination. Safflower oil is a household cooking oil (a triglyceride) that is distinguished by the carbonyl bands at  $1735\text{ cm}^{-1}$  and additional bands at lower wavenumbers. Like the aliphatic hydrocarbon stretching band, this carbonyl band is another excellent indication of organic contamination. This band alone is not sufficient to identify the stain as a vegetable oil. The small band at  $3011\text{ cm}^{-1}$  indicates that it is an unsaturated oil. Silicone oil (Dow Corning DC200-5cps) is easily distinguished from mineral and vegetable oils by the shape of the band near  $3000\text{ cm}^{-1}$  (Silicone has only methyl hydrogens), the Si-C band at  $1265\text{ cm}^{-1}$ , and the Si-O bands near and below  $1000\text{ cm}^{-1}$ . The Hershey cocoa butter soap is an example of a soap made by the saponification of triglycerides, resembling the safflower oil spectrum with the exception that the carbonyl band is shifted to lower wavenumbers because it is now a carboxylic acid. The broad bands near  $3400\text{ cm}^{-1}$  seen to some extent in all these spectra results from hydroxyl species, usually due to water in or under the films or due to alcohols in the stain. A general rule of thumb is that an 0.1 a.u. response corresponds to a film thickness for the stain of approximately one micron (100 milligrams per square foot) although the surface texture may affect the exact value of the stain film thickness considerably. Comparing Figure 3 (the system signal-to-noise) the common stains in Figure 4, shows that



**Figure 4.** Library spectra obtained using smear stains on sandblasted steel, showing the unique patterns of common surface contaminants. These spectra represent film thickness on the order of one micron (100 milligram per square foot).

it is possible to detect an infrared response for contamination that is 1000 times less than the thickness of commonly occurring stains. Very elegant statistical algorithms now exist to search out and identify these library spectra with little operator intervention.

Figure 5 shows three spectra of suspected contaminants for which a chemical analysis was not immediately available. The rinse water concentrate is from a rinse bath that was thought to be approaching its limit for accrued detergent. The concentrate was placed on sandblasted aluminum and allowed to evaporate. The fingerprint spectrum was obtained from a fingerprint smudge applied to sandblasted aluminum. The unknown oil was an oil droplet found on a black oxide steel gear component. It was smudged onto sandblasted aluminum to make this library spectrum. The oil is clearly an aliphatic hydrocarbon ester with



**Figure 5. Library spectra obtained using smear applied stains on sandblasted aluminum, demonstrating the unique patterns of surface contaminants suspected to be contributors to contamination on black oxide finished steel gears.**

other distinct bands. A search of a large commercially available library would probably identify this oil by its commercial name. The point to be made thus far is that surface inspection depends strongly on knowing what to look for. Library development is a critical part of this inspection process. Libraries should be developed to include the likely contaminants while not overloading the library with unlikely candidates.

### 3.2 INSPECTION OF BLACK OXIDE STEEL GEAR PARTS

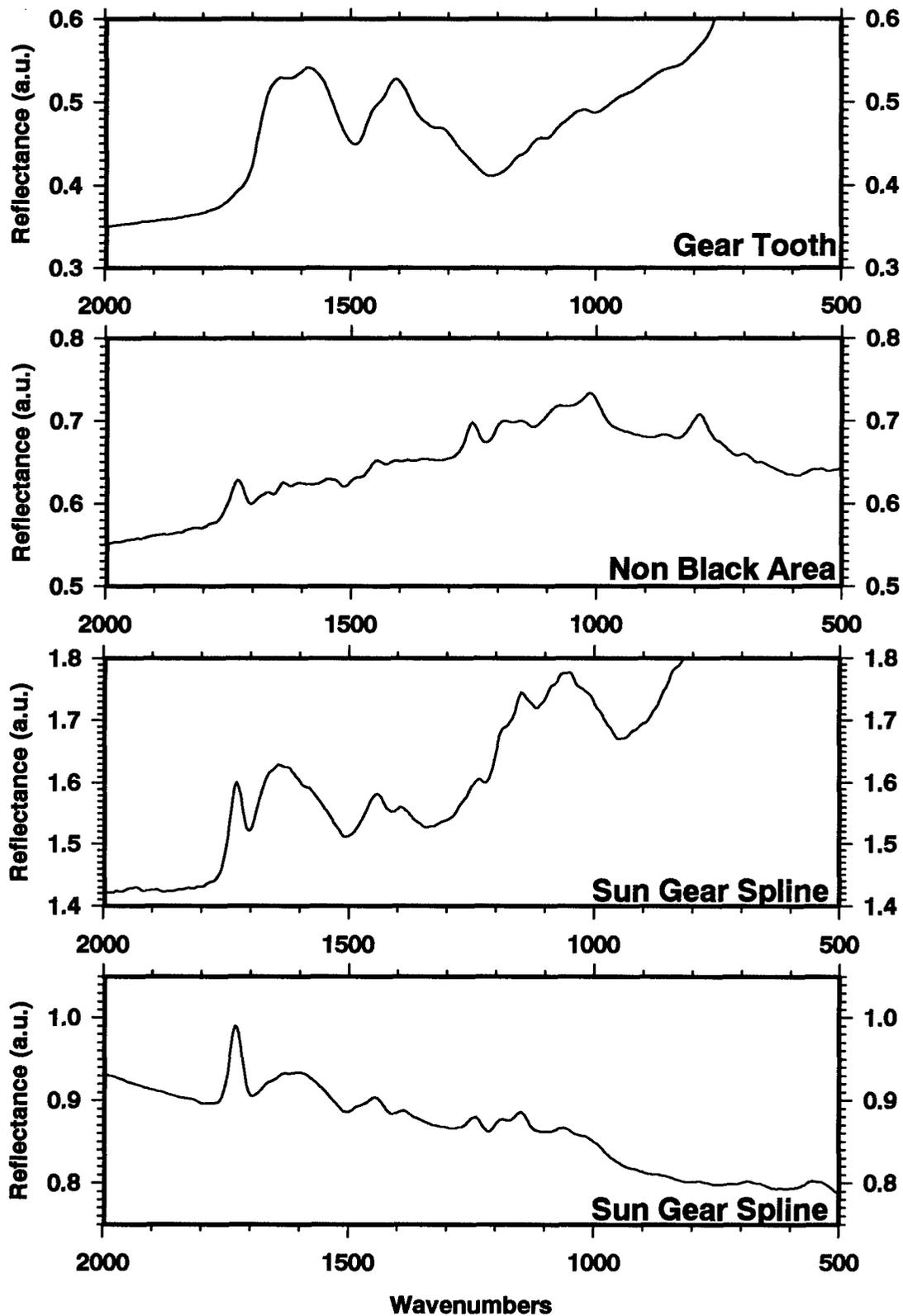
As part of the introduction of the CCAD to the SOC 400 SIMIR, a number of black oxide finished steel gear parts were analyzed. This was in part an exercise in inspecting large objects of peculiar shapes, and in part as an exercise in inspecting surfaces that were neither flat nor sandblasted. Figure 6 shows data obtained from several locations of these parts. Gear teeth were among the easier surfaces to address with the SOC 400. The gear tooth spectrum (Figure 6) appears to represent the infrared absorption spectrum of black oxide finish on a relatively clean steel gear. These are broad bands between 1700 and 1400  $\text{cm}^{-1}$  that appeared to vary in relative intensity from part to part and place to place on the same part. This is supported by the fact that spectra from the non-black area (an area where the oxide had been worn off) did not demonstrate these bands. The non-black area did show evidence for an aliphatic ester contaminant. This contaminant was observed on a number of other parts as indicated by two examples obtained from a sun gear spline area. This contaminant was first thought to be the unknown oil shown in Figure 5, but closer examination indicated that all the bands from the unknown oil (Figure 5) could not be found. This exercise did demonstrate that the presence of organic contaminants could be found on ordinary metal parts under conditions where the presence of this contamination could not be detected visually.

### CONCLUSIONS

A small, user friendly, light weight, field hardened, computer controlled device for performing surface inspection based on infrared spectroscopic analysis, with high sensitivity of trace contamination on surfaces, is now available for detecting surface contamination, particularly organic contamination on metals. The SOC 400 SIMIR brings to the workplace an inspection capability for detecting trace amounts of contamination on metal surfaces that may otherwise go undetected. The SOC 400 SIMIR is supported by a tremendous existing base in science and technology for use in certifying the cleanliness of metal surfaces at levels that have not been previously available. The job remaining is to develop the practice of the practical inspection of real parts based on a sound knowledge of potential contaminants and their qualitative and quantitative analytical determination.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge B. H. Nerren, National Aeronautics and Space Administration, Marshall Space Flight Center, Alabama, for his efforts to implement this inspection technology; T. E. Barber, Sam Houston State University, Huntsville, Texas for his efforts developing spectral mapping technology, and to J. T. Neu and the staff at Surface Optics Corporation, San Diego, California for their excellent work in fielding the SOC 400.



**Figure 6.** Spectra obtained from black oxide finished steel gear parts. The broad bands appear to be features of the black oxide and their relative intensities. Contamination by an aliphatic ester oil was detected as the 1735  $\text{cm}^{-1}$  band.

## REFERENCES

- <sup>1</sup>G. L. Powell, M. Milosevic, J. Lucania, and N. J. Harrick, "The Spectropus System, Remote Sampling Accessories for Reflectance, Emission, and Transmission Analysis using Fourier Transform Infrared Spectroscopy," *Appl. Spectrosc.* **46**, 111-125 (1992).
- <sup>2</sup>G. L. Powell, N. R. Smyrl, D. M. Williams, H. M. Meyers, III, T. E. Barber, M. Marerro-Rivera, "Surface Inspection Using Fourier Transform Spectroscopy," *Aerospace Environmental Technology Conference, NASA Conference Publication 3298*, A. F. Whitaker, ed., MSFC, Alabama, 563-571 (1995).
- <sup>3</sup>G. L. Powell, T. E. Barber, M. Marrero-Rivera, D. M. Williams, N. R. Smyrl, and J. T. Neu, "Oil Analysis on Metal Surfaces using DR-FTIR Mapping Techniques", *Micrichimica Acta*, in press.
- <sup>4</sup>G. L. Powell, "The Determination of LiOH on LiH by Diffuse Reflectance Fourier Transform Infrared Spectroscopy," *Reflections*, N. J. Harrick, ed., Harrick Scientific, Inc., Ossining, NY (1990).
- <sup>5</sup>G. L. Powell, N. R. Smyrl, C. J. Janke, E. A. Wachter, W. G. Fisher, J. Lucania, M. Milosevic, and G. Auth, "Nondestructive Inspection of Graphite-Epoxy Laminates for Heat Damage using DRIFT and LPF Spectroscopies," in *The Proceedings of the Conference on Characterization and NDE of Heat Damage in Graphite Epoxy Composites, NTIAC*, Austin, Texas, 97 - 111 (1993).
- <sup>6</sup>G. L. Powell, T. E. Barber, and J. T. Neu, "Instrumentation for the Determination of Material Properties from Spectroscopic Measurements of Total Integrated Scatter," *Proceedings of SPIE's 40th Annual Meeting and International Symposium on Optical Science, Engineering, and Instrumentation 2541*, J. C. Stover, ed., Bellingham, Washington, 142 - 153 (1995).