NEAR INFRARED DIFFUSE REFLECTANCE STANDARDS[1]

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ABSTRACT

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Diffuse reflectance characteristics were examined for sulfur, polytetrafluoroethylene (PTFE), a mixture of sulfur and PTFE, MgO, smoked MgO, $BaSO_4$, fused Teflon, ceramics, kaolin, opal glass, aluminum, brass, and gold in the 1.0–2.6-μ region. Sulfur pressings gave the highest, most uniform reflectance of all materials examined. Thus, sulfur is a suitable material as a reflectance standard in the near infrared region.

For investigations of near infrared reflectance characteristics of cereals, a reflectance standard must be used that has a high, uniform diffuse reflectance in the 1.0–2.6-μ region. Compounds hitherto used as reflectance standards for near infrared reflectance are those usually used for the visible region, namely, magnesium oxide (smoked and as a pressed powder) and pressings of barium sulfate (1–7). These compounds are unsuitable as near infrared standards, however, due to the presence of water peaks, instability, and low reflectance. Other materials that have been suggested as suitable for reflectance standards or as coatings for integrating spheres in the near infrared region are alumina (8), polytetrafluoroethylene (PTFE) powder (9), flowers of sulfur (10–12), and opal glass (13). This article reports on the relative diffuse reflectance of the above materials and recommends the use of pressings of sulfur as a working reflectance standard in the 1.0–2.6-μ region.

MATERIALS AND METHODS

Reflectance Measurements

Reflectance spectra were recorded between 1.0 and 2.6 μ using a Cary 17I spectrophotometer as described previously (14), except the interior of the integrating sphere was coated with gold instead of smoked MgO, and pressings of sublimed sulfur were used as a reflectance standard instead of smoked MgO. Optical geometry of the sphere used in this study was 0°/d.

Preparation of Materials

The source and description of materials studied are listed in Table I.

All pressings of sulfur, PTFE powders, and a mixture of sulfur and PTFE were compressed to a thickness of 6 mm using a Carver laboratory press at 18, 88, 211, and 350 kg/cm^2 and a 57-mm diameter die. Before compressing, sulfur and PTFE (9:1, w/w) were thoroughly homogenized in a Krups grinder for 1 min. This mixture is referred to as Sulfon.

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TABLE I
Source and Description of Materials Used in Reflectance Study

Material	Source	Description
Sulfur	Fisher Scientific, Pittsburgh, PA	Sublimed, laboratory grade, S-591
MgO (smoke) (Mg ribbon)	Matheson, Coleman and Bell, Norwood, OH	MgO smoke by thermal deposition
MgO (powder)	J. T. Baker Chemical Co., Phillipsburg, NJ	Ultrex, No. 4903, 99.9%
MgO (powder)	J. T. Baker Chemical Co., Phillipsburg, NJ	Analytic reagent, 99.7%
$BaSO_4$	Eastman Kodak Co., Rochester, NY	White reflectance standard
PTFE[a]		
Teflon 7A	E.I. du Pont de Nemours, Wilmington, DE	Round particles, 35-μ diam., 475 g/L
Teflon 7B	E.I. du Pont de Nemours, Wilmington, DE	Round particles, 25-μ diam., 375 g/L
Teflon 7C	E.I. du Pont de Nemours, Wilmington, DE	Stringy particles, ca. 30 μ, 275 g/L
Teflon 8	E.I. du Pont de Nemours, Wilmington, DE	Round particles, 600-μ diam., 720 g/L
Hostaflon TF	Farbwerke Hoechst A. G., Frankfurt, Germany	Properties unknown
PTFE (sheet)	Johnston Industrial Plastics, Winnipeg, Man.	Commercial grade, 3 and 13 mm
PTFE (standard)	Neotec Instruments, Inc., Silver Spring, MD	Reflectance standard, 50 × 50 × 3 mm
Opal glass	National Physical Laboratory, Teddington, England	Russian-type MS-20, 50 × 50 × 10 mm
Kaolin (powder)	J. T. Baker Chemical Co., Phillipsburg, NJ	Hydrated aluminum silicate (technical grade)
Ceramic (standard)	Neotec Instruments Inc., Silver Spring, MD	Reflectance standard
Ceramic (standard)	Technicon Industrial Systems, Tarrytown, NY	Reflectance standard
Aluminum (foil)	Obtained locally	Commercial grade, household
Aluminum (plate)	Obtained locally	Commercial grade, 9 mm
Brass (plate)	Obtained locally	Commercial grade, 6 mm
Gold (wafer)	Bank of Nova Scotia, Winnipeg, Man.	10 g, 99.99% purity

[a] PTFE = polytetrafluoroethylene.

MgO powder was compacted by hand and also compressed with a polished stainless steel ram at 200, 400, and 800 kg/cm^2 in a well (38 mm in diameter, 6 mm deep) recessed in an aluminum block. Samples of smoked MgO were prepared by first compressing a 5-mm layer of MgO powder in an aluminum well and then covering it with a 1-mm layer of smoked MgO.

$BaSO_4$ was compacted into an Eastman acrylic holder according to the manufacturer's instructions, ie, 2 g/cm^3; also, $BaSO_4$ was compressed in an aluminum well with a polished stainless steel ram at 800 kg/cm^2.

Kaolin (hydrated aluminum silicate) disks were prepared by packing a slip made from the powder and water into a mold (38 mm in diameter, 6 mm thick) and then drying one at 50°C for five days and one at 1,200°C for 16 hr.

Opal glass was a Russian-type MS-20 special photometric glass from National Physical Laboratory,[4] 50 × 50 × 10 mm, having one major face ground flat and polished.

Blocks of aluminum and brass were sanded in a circular or unidirectional motion using from coarse (No. 60) to fine (No. 600) silicon carbide sandpaper.

A commercial 10-g wafer of gold (99.99% purity) was roughened with No. 120 silicon carbide sandpaper. Gold evaporated in high vacuum (10^{-5} torr) on glass plates, polished, or sandblasted aluminum blocks was also examined.

RESULTS AND DISCUSSION

Spectrophotometric adjustments were made to obtain a spectral recording for sulfur pressing versus sulfur pressing as a straight line at 100% diffuse reflectance from 1.0–2.6 μ. Spectral recordings for all materials listed in Table I relative to sulfur are shown in Fig. 1–12. Reflectance values for sulfur relative to absolute data for smoked MgO are presented in Table II and compared with values of Kronstein et al (10) in Table III. Reflectance characteristics for sulfur are shown to be higher than for all materials reported in this work.

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[4] F. J. J. Clarke. Personal communication.

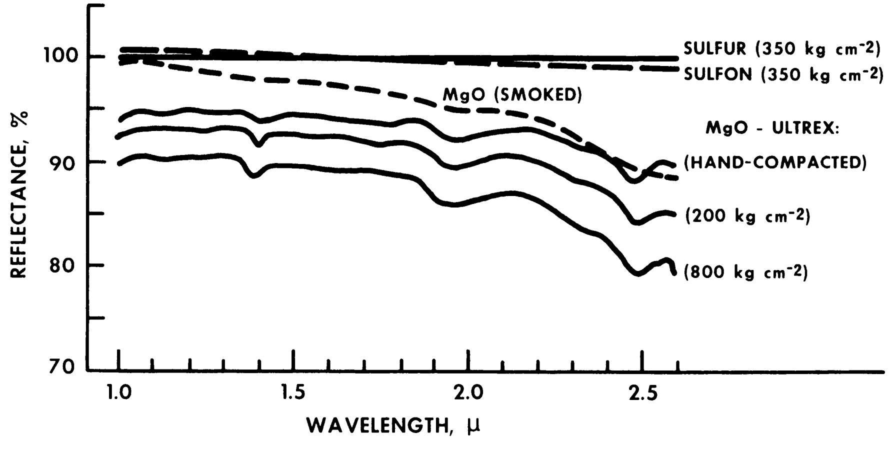

Fig. 1. Diffuse reflectance (versus sulfur pressing) of Sulfon, smoked MgO, and MgO Ultrex powder compacted by hand and compressed at 200 and 800 kg/cm^2 of pressure.

In Fig. 1, a comparison of the recordings for sulfur and Sulfon pressed at 350 kg/cm^2 shows that addition of 10% PTFE to sulfur (to form Sulfon) has only a small effect on the reflectance of sulfur as seen by the slight increase above and

TABLE II
Reflectance Values for Sulfur

Wavelength (μ)	Sulfur[a]	Sulfur[b]	Smoked MgO[c]	$BaSO_4$[c]
1.0	97.5	97.5	97	99.2
1.1	98	97	97	99
1.2	97	96.5	96	98
1.3	97.5	96.5	96	98
1.4	97.5	96.5	94.5	95.5
1.5	98	96.5	95.5	95.5
1.6	98	96.5	95	96
1.7	97	96	94	95.5
1.8	97.5	96	94	94
1.9	98	96.5	93	90.5
2.0	97.5	96	92.5	90
2.1	98	96.5	92.5	91
2.2	98	96	92	90.5
2.3	99	97	91	90.5
2.4	98.5	97	90	88.5
2.5	98	96.5	87	85

[a] Values for this study based on absolute data for smoked MgO published by Morren et al (7).
[b] Values for this study based on absolute data for $BaSO_4$ pressed powder published by Morren et al (7).
[c] Absolute values published by Morren et al (7).

TABLE III
Comparison Between Two Sets of Reflectance Values for Sulfur

Wavelength (μ)	Sulfur[a]	Sulfur[b]	Smoked MgO[c]
1.0	96.3	89.1	95.8
1.1	96.6	90.1	95.6
1.2	96.5	89.8*	95.3
1.3	96.7	90.3	95.2
1.4	97.9	90.9*	94.9
1.5	97.7	91.0	95.1
1.6	97.8	91.3*	95.0
1.7	98.1	91.7*	94.9
1.8	98.2	92.3*	94.6
1.9	99.2	93.3*	94.1
2.0	99.4	94.2	94.2
2.1	99.7	94.2*	94.2
2.2	100.7	95.4	94.2
2.3	101.5	96.9*	93.4
2.4	102.1	98.0*	93.3
2.45	105.0	99.5	94.0

[a] Values for this study based on data for smoked MgO published by Sanders and Middleton (2).
[b] Values for sulfur published by Kronstein et al (10), based on data for smoked MgO published by Sanders and Middleton (2). Asterisk indicates values calculated from data of Kronstein et al (10).
[c] Absolute values published by Sanders and Middleton (2).

decrease below 1.7 μ. Sulfon has the advantage over sulfur in that it forms a more rigid pressing, and also that it is easy to machine in a lathe. The disadvantage, however, is that after repeated use, Sulfon takes on a slight glossy appearance, a factor that is undesirable for diffuse reflectance.

Recordings for MgO and $BaSO_4$, which Erb (15) describes as two materials most widely used for reflectance standards, are shown in Fig. 1 and 2. Smoked MgO, compressed MgO powders, and compressed $BaSO_4$ show a decrease in reflectance toward the longer wavelengths. Also, an increase in pressure on MgO and $BaSO_4$ powders results in a lowering of their reflectance, an effect that Schatz (16) also showed for these and other powders. Water peaks, at approximately 1.45 and 1.93 μ, are noted in the recordings for both MgO and $BaSO_4$ powders. Other peaks are shown for MgO powders (Fig. 1), which are more pronounced when MgO powder of lower purity was used (Fig. 3).

A comparison of smoked MgO and $BaSO_4$ with sulfur is shown in Table II. Reflectance values for sulfur were obtained by using smoked MgO, or $BaSO_4$ as reference standards. The values are based on the absolute data published by Morren et al (7). Values for sulfur relative to smoked MgO are shown to be quite uniform (97–99%) over the entire wavelength range. The absolute values for smoked MgO are similar to the relative values for sulfur only at 1.0 μ and then progressively decrease to 87% at 2.5 μ. A similar comparison between $BaSO_4$ and sulfur shows consistent uniformity for sulfur, however, at a slightly lower level (96–97.5%). $BaSO_4$ values are higher than for sulfur from 1.0 to 1.3 μ, but decrease steadily from 1.4 to 2.5 μ.

In Table III, reflectance values for sulfur are compared with those of Kronstein et al (10), both being relative to the same absolute values for smoked MgO that Sanders and Middleton (2) published. Our values for sulfur are higher than these absolute values for smoked MgO from 1.0 to 2.45 μ; those of Kronstein et al (10) are lower below 1.9 μ and higher from 2.0 to 2.45 μ. The reason for the

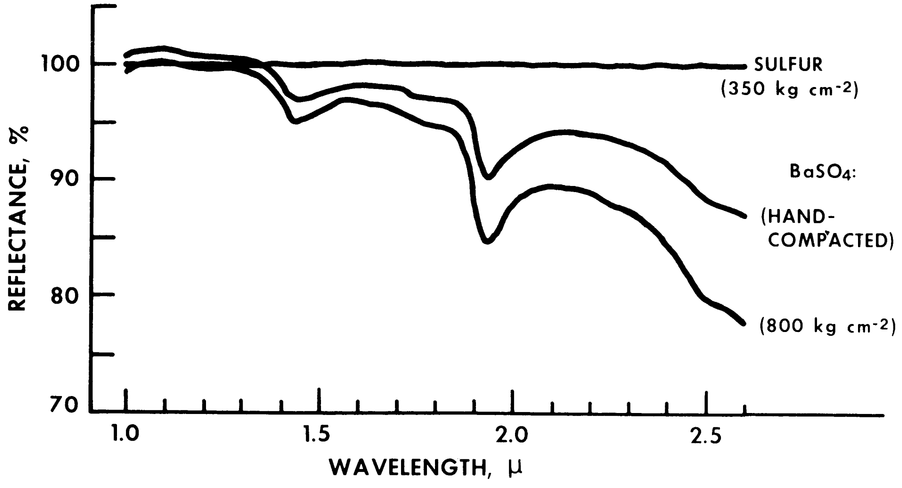

Fig. 2. Diffuse reflectance (versus sulfur pressing) of $BaSO_4$ compacted by hand and compressed at 800 kg/cm^2 of pressure.

discrepancy in reflectance of 4–8% between our values for sulfur and those of Kronstein et al (10) is not known. Perhaps different methods of preparation or varying purity of the sulfur pressings and smoked MgO reference standards account for these differences.

Based on the absolute values for smoked MgO and $BaSO_4$ that Grum and Luckey (6) published, the results for sulfur (not shown) are markedly different from those that were previously based on absolute values that other authors (2,7) gave. The effect on the sulfur values is shown as a significant decrease in reflectance at longer wavelengths and at 1.45 and 1.93 μ. These results indicate that existing reflectance values for sulfur powder are unreliable. This situation is

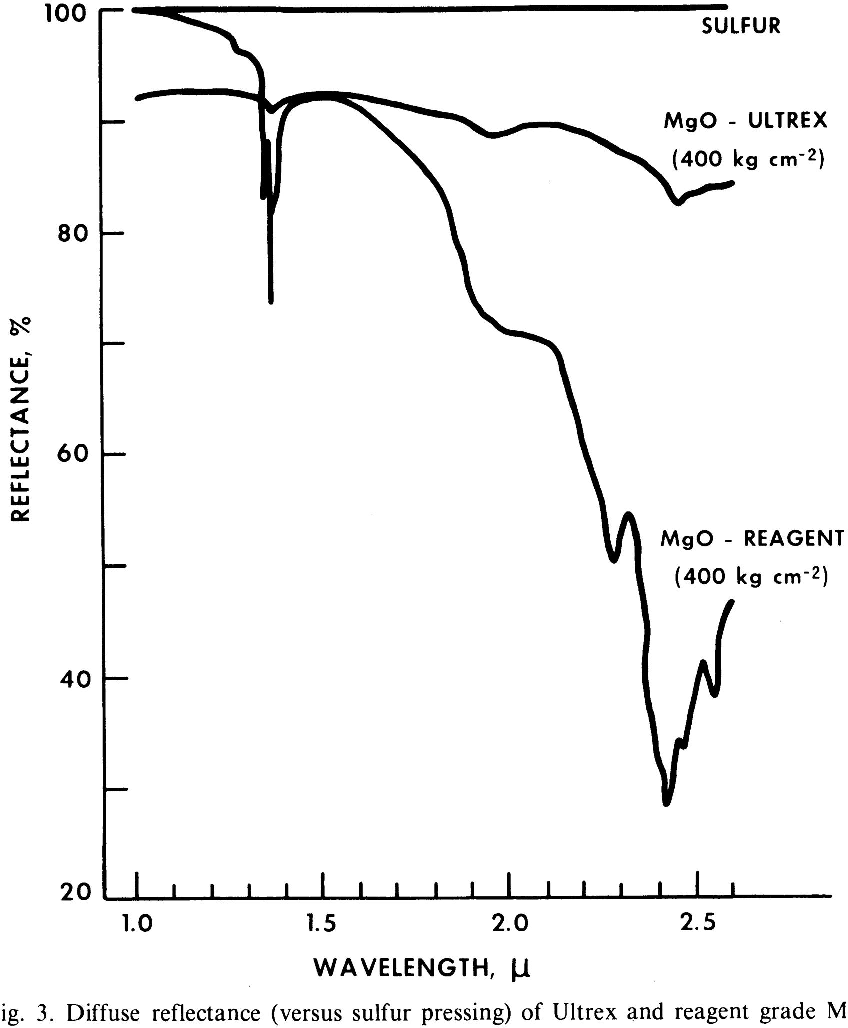

Fig. 3. Diffuse reflectance (versus sulfur pressing) of Ultrex and reagent grade MgO powders compressed at 400 kg/cm^2 of pressure.

unsatisfactory, and suggests that national laboratories should determine the absolute reflectance values for sulfur.

Of the PTFE powders studied, namely, Teflon 7A, 7B, 7C, 8, and Hostaflon TF, Teflon 7B and Hostaflon TF exhibit the highest reflectance. The results in Fig. 4 support Hoffmann's (9) conclusion that Hostaflon TF has an absolute reflectance of greater than 95% over the range 1.0–2.0 μ. Above 2.0 μ, the reflectance of all PTFE-compressed powders decreases sharply due to the C-H groups of the absorption band at 2.14 μ. The three curves for Teflon 7B pressings indicate that reflectance decreases markedly with increasing pressure, an effect that Schatz (16) previously showed for metal and oxide powders. Moreover, specular reflection of all PTFE pressings increases noticeably with increase in pressure.

In Fig. 5, curves for commercial fused PTFE (Teflon) show an even lower reflectance than for Teflon 7B at the highest pressure shown in Fig. 4. Again the peak at 2.14 μ is observed. Lower reflectance caused by the transparency of fused PTFE is shown by comparing the results for 3-, 13-, and 39-mm thick plates.

Curves for Neotec Teflon standards backed by aluminum foil (Fig. 6) show a higher reflectance than when backed by Bakelite. Curves for two standards examined separately are similar to each other, but have slightly different

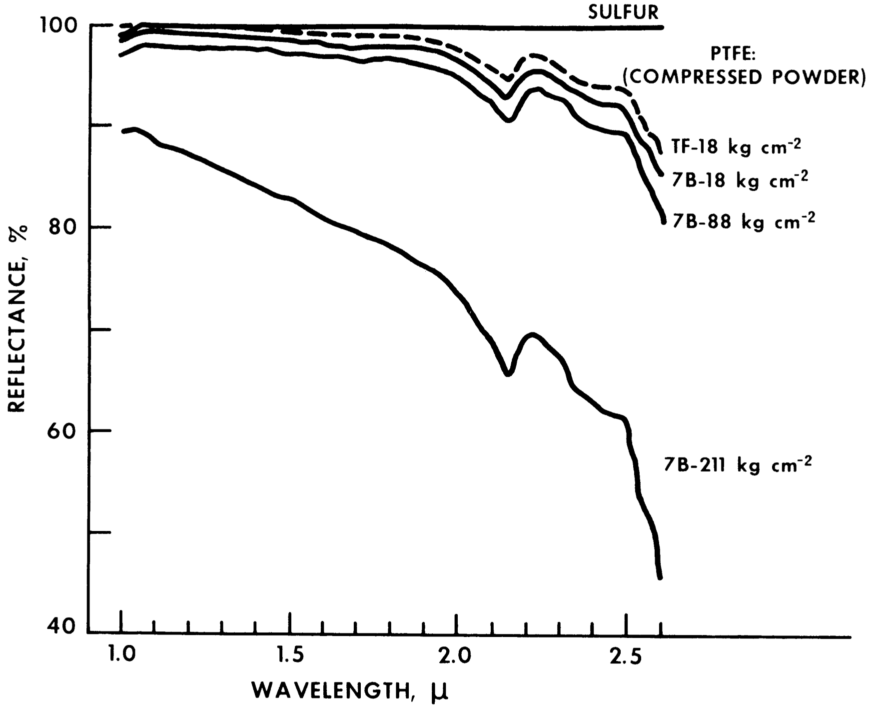

Fig. 4. Diffuse reflectance (versus sulfur pressing) of polytetrafluoroethylene (PTFE) powders: Hostaflon TF compressed at 18 kg/cm^2 of pressure; Teflon 7B compressed at 18, 88, and 211 kg/cm^2 of pressure.

reflectances (Fig. 6). When the two Teflon standards are placed together, a lower reflectance is obtained. These results show again that fused Teflon is transparent to near infrared radiation, indicating that it is an unsatisfactory material for a reflectance standard.

Ceramic materials are presently used as reflectance standards in some commercial near infrared reflectance instruments. Recordings for these standards (Fig. 7) are fairly uniform over the 1.0–2.6-μ range, showing only a small peak at 2.21 μ. The reflectance of both standards (between 83 and 90%), however, is much lower than for sulfur. Also, matt-surfaced ceramics, being porous, tend to trap both dust and light into the pores, thereby lowering their reflectance.

Significant transmission and diffusion of light inside opal glass makes it unsuitable as a diffuse reflectance standard (13). Also several peaks, at approximately 1.4, 1.9, and 2.2 μ, are noted in the curve recorded for opal glass (Fig. 7). Moreover, reflectance falls off quite sharply in the 2.0–2.6-μ region.

Reflectance of a ceramic material prepared by heating kaolin slip at 50°C or fusing it at 1,200°C is shown in Fig. 8. The higher temperature treatment results in a virtual disappearance of the large peaks exhibited by the kaolin dried at the

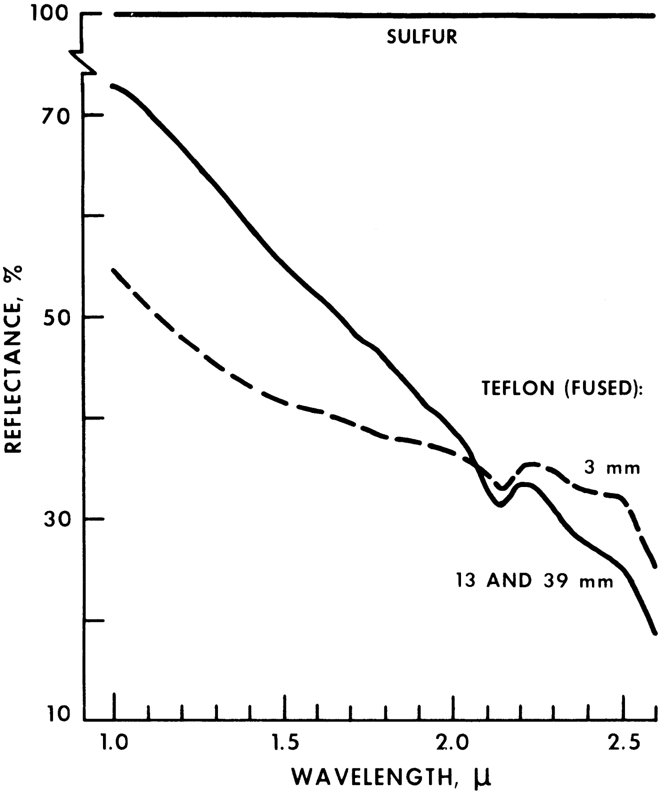

Fig. 5. Diffuse reflectance (versus sulfur pressing) of fused Teflon (3, 13, and 39 mm thick).

lower temperature of 50°C. Reflectance (95–99%) is much higher for kaolin fused at 1,200° C. It may be possible to fuse kaolin slip above 1,200° C to produce satisfactory ceramic reflectance standards of uniform and high reflectivity.

Metals such as aluminum or brass are not well suited for reflectance standards, since a large variability in reflectance is obtained depending on the type of surface used (as shown for aluminum in Fig. 9 and 10). Highly polished surfaces, eg, shiny aluminum foil, give low diffuse reflectance, indicating the presence of a significant specular component. The smooth and shiny surfaces also show a decrease in reflectance with increase in wavelength (Fig. 9). Rough and dull surfaces, however, eg, aluminum roughened with coarse sandpaper or sandblasted, show an increase in reflectance with increase in wavelength (Fig. 10).

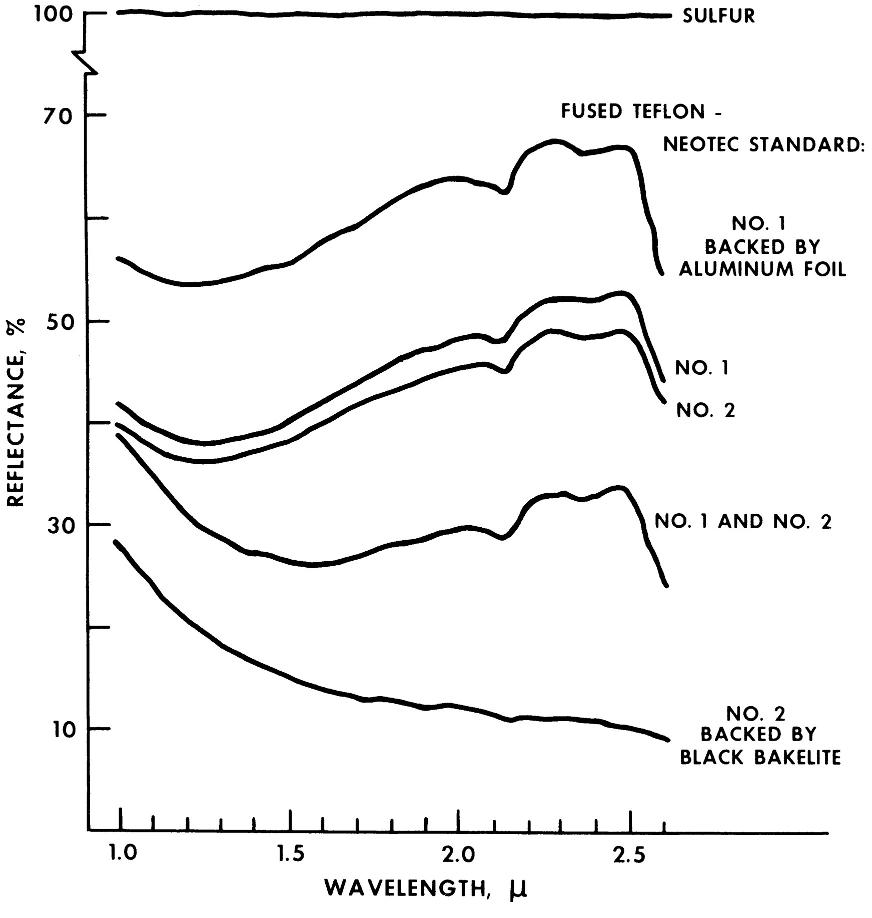

Fig. 6. Diffuse reflectance (versus sulfur pressing) of fused Teflon (Neotec reflectance standards). Curves are shown for two standards examined separately and together, placed front to back; also for one standard backed by aluminum foil and another by black Bakelite.

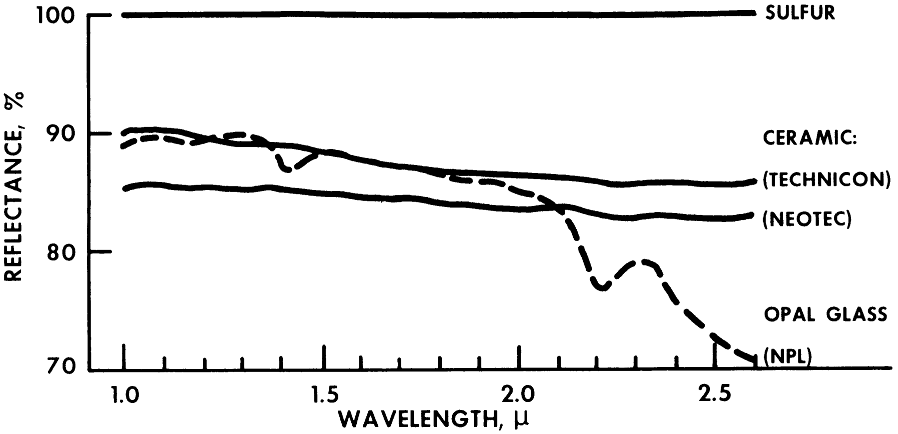

Fig. 7. Diffuse reflectance (versus sulfur pressing) of ceramic reflectance standards used by Technicon and Neotec, and of opal glass, type MS-20, from National Physical Laboratory.

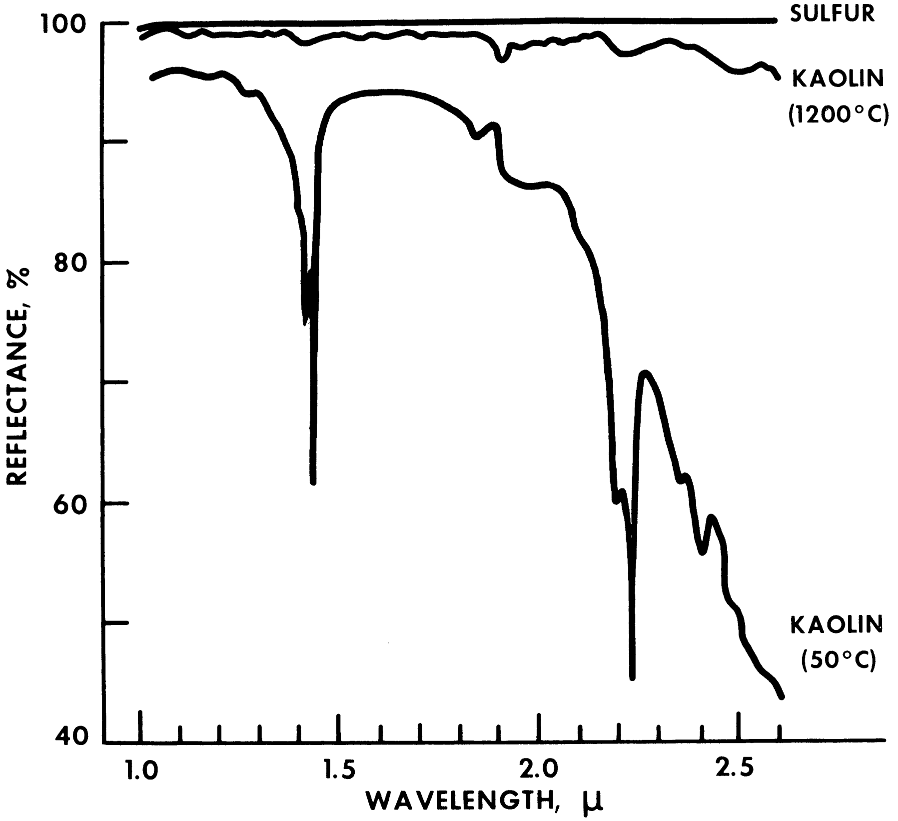

Fig. 8. Diffuse reflectance (versus sulfur pressing) of kaolin slip dried at 50° C for five days and fused at 1,200° C for 16 hr.

Another type of variation in surface reflection is illustrated in Fig. 11, in which brass plate, unidirectionally grained with coarse sandpaper (No. 60), was examined at the horizontal, vertical, or 45-degree position (with respect to the sphere port). The results show the highest reflectance for the horizontal, lowest for the vertical, and midpoint between the two for the 45-degree position of the brass plate. Dunkle (17) noted that with the surfaces rough and grained, more energy is reflected to the detector in some positions than in others. This phenomenon demonstrates, in part, the complexity of surface reflections of metals. Aluminum surface roughened in the same manner as brass gave similar reflectance values (results not shown). In addition to surface variation, these metals are also chemically reactive, forming various oxides in laboratory atmospheres. The observed numerous significant differences in the reflection of chemically reactive metals indicate that they are not suitable as reflectance standards.

Reflectance curves for gold with different surfaces are shown in Fig. 12. Gold-coated glass has a low diffuse reflectance and a high specular component. Gold-coated polished aluminum is similar in reflectance to aluminum polished with fine (No. 600) sandpaper. Reflectance of sandblasted aluminum was not altered

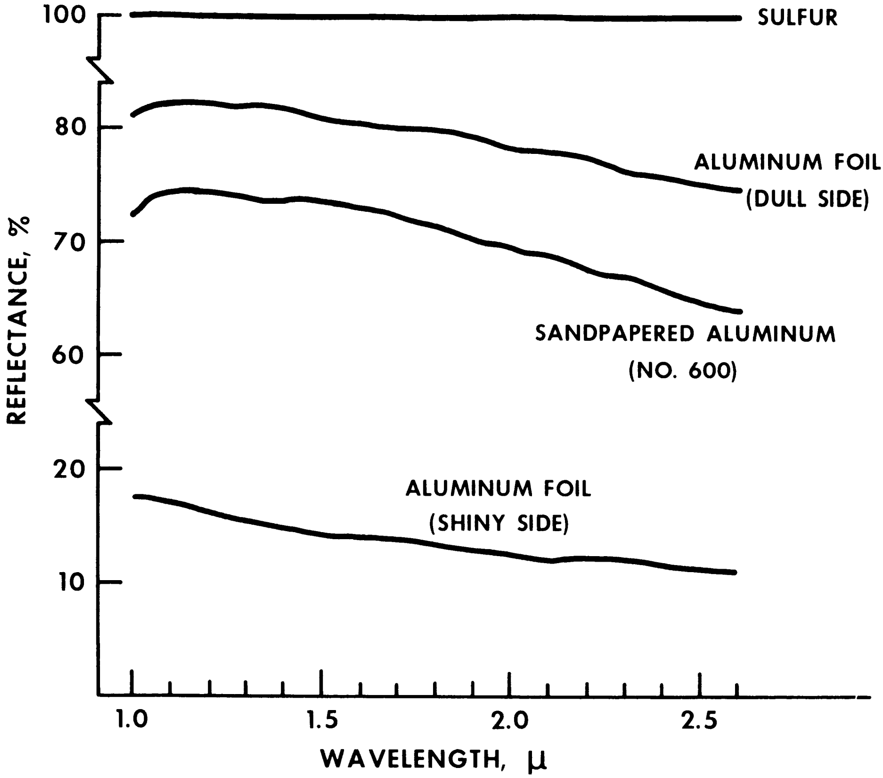

Fig. 9. Diffuse reflectance (versus sulfur pressing) of smooth and polished surfaces of aluminum: shiny and dull foil; block polished with fine (No. 600) silicon carbide paper.

by vacuum deposition of gold on its surface. Sandpapered gold wafer shows highest reflectance (85–88%) as compared with all gold surfaces illustrated in Fig. 12. The curve for this gold wafer has no peaks and is quite uniform throughout the entire wavelength range, which is in agreement with a report by Shaw (18). The advantage of using gold as a reflectance standard is that it is

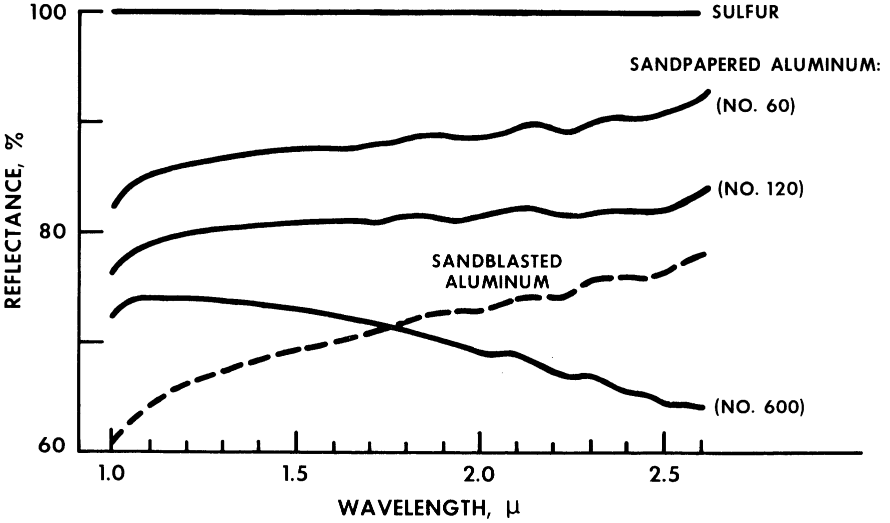

Fig. 10. Diffuse reflectance (versus sulfur pressing) of rough and dull surfaces of aluminum blocks prepared by sanding in circular motion with coarse (No. 60), medium (No. 120), or fine (No. 600) silicon carbide paper or sandblasting.

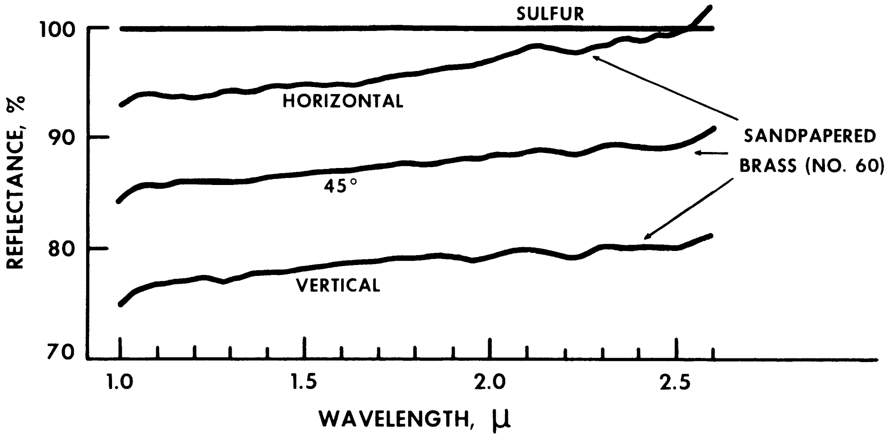

Fig. 11. Diffuse reflectance (versus sulfur pressing) of brass plate unidirectionally sanded with coarse (No. 60) silicon carbide paper. Sanded plate was rotated so that grain was in horizontal, vertical, or 45-degree position with respect to sample port of integrating sphere.

stable as compared with other metals. Bennett and Ashley (19), using gold evaporated in ultrahigh vacuum, showed that it keeps its high reflectance indefinitely. Some disadvantages, however, are that it is soft and expensive. Other types of gold surfaces, such as Lambertan surface gold-plated aluminum,[5] may be satisfactory reflectance standards, but we were unable to examine these products.

CONCLUSIONS

Sulfur pressings show the best reflectance characteristics of all the materials examined in this study. Examination of three different samples of sublimed sulfur[6] showed results similar to those described in this study. No change in

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[5] Sold by Cohan-Epner Co., Inc., 55 Meadow Street, Brooklyn, NY.

[6] Two lots of laboratory grade from Fisher Scientific, Pittsburgh, PA, and one lot of U.S.P. grade from Mallinckrodt Chemical Works, St. Louis, MO.

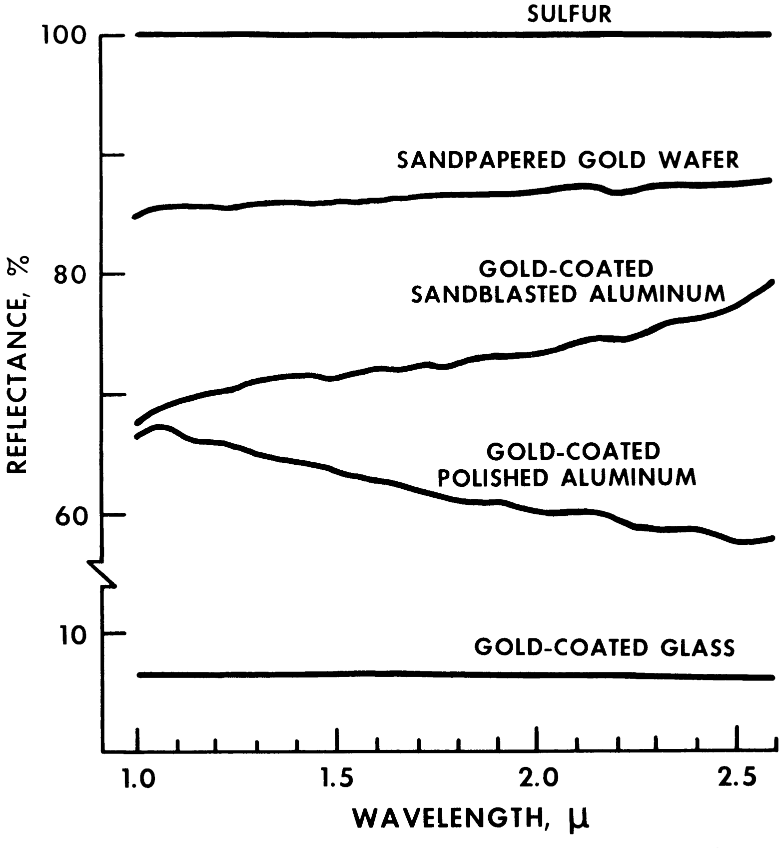

Fig. 12. Diffuse reflectance (versus sulfur pressing) of gold surfaces: gold wafer roughened with medium (No. 120) silicon carbide paper; gold-coated sandblasted aluminum; gold-coated polished aluminum (with fine, No. 600 paper); gold-coated glass plate.

reflectance was observed due to increase in compaction of sulfur pressings up to 350 kg/cm^2. Alteration of sphere geometry to include specular component made no change in reflectance of these pressings. The reflectance of sulfur pressings used for two years did not change, which indicates they are stable. Sulfur pressings are not as strong as ceramic discs, however, and may not withstand laboratory accidents as well. For example, if dropped, a sulfur standard would tend to break more easily than would a ceramic standard.

Erb (15) recently listed the ideal properties of reflection standards as transportable, homogeneous smooth surface, diffuse reflecting, spectrally nonselective, nontransparent, nonfluorescent, and easy to handle. Sulfur pressings are superior or equal to the other near infrared reflectance standards in all properties that Erb (15) listed. Consequently, these pressings can be useful to workers in the field of near infrared spectroscopy.

Acknowledgments

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