TABLE I. **Ratio of peak heights of the urethane amide II carbonyl at 1530 cm^{-1} to the Phenoxy® aromatic stretch at 1510 cm^{-1}.**

Sample	Ratio
Standard mixture of urethane/Phenoxy®	1.2:1.0
Urethane, then Phenoxy®	0.3:1.0
Phenoxy®, then urethane	1.1:1.0

of the oxide. The upper spectrum is the composite of oxide/Phenoxy PKHH®, the middle spectrum is that of the *gamma*-iron oxide, and the bottom spectrum is that of the composite after subtraction of the *gamma*-iron oxide. Figure 6 is the expansion spectrum of Fig. 5c, and is in good agreement with the transmission spectrum of Phenoxy PKHH®.

To determine the preference of the oxide for the Estane 5703® or the Phenoxy PKHH®, we carried out two separate studies. The first was done by equilibrating separate samples of the oxide with either of the two adsorbates and then re-equilibrating the oxide with a solution of the other adsorbate before decanting, drying, and analyzing. The peak-to-height ratio on the FT-IR/PAS spectra of the two compounds was calculated according to the absorbances of the two peaks at 1530 and 1510 cm^{-1}. This ratio was then compared to the ratio of the same two peaks in a solution made by combining volumes equal in size to those used for the original equilibrations, but without the oxide. The infrared spectrum of this mixture was obtained by depositing a drop of the sample onto the surface of a KBr plate. If the peak height ratio of the adsorbed polymers on the *gamma*-iron oxide is equal to that of the polymers in the standard solution, the polymers are equally adsorbed. Any change in this ratio would suggest an oxide preference for one of the polymers over the other. Table I shows that there is an oxide adsorption preference for the Phenoxy PKHH®, as the peak height ratios of the adsorbed polymers are both smaller than that of the standard mixture.

In the second study the equilibration was made from a single solution which contained equal volumes of the adsorbate solutions used in the above study. The *gamma*-iron oxide was added to this solution, which was then shaken for 72 h, allowed to settle, decanted, and washed, and the FT-IR/PAS spectrum obtained. The Estane® to Phenoxy® ratio was calculated from the 1530-cm^{-1} and 1510-cm^{-1} bands, and the results are shown in Table II. Again the ratio has changed, showing that the Phenoxy PKHH® is the adsorbate of choice; i.e., the peak-to-height ratio decreased from that of the standard solution.

SUMMARY

It is possible to obtain infrared spectra of Estane 5703® and Phenoxy PKHH® adsorbed onto the surface of *gamma*-iron oxide by FT-IR/PAS. Although the *gamma*-iron oxide absorbances contribute to the overall infrared spectrum, when substracted from the composite spectrum the infrared spectrum of the polymer is the result. The FT-IR/PAS spectra of the Estane 5703® and Phenoxy PKHH® are in good spectral agreement with transmission spectra obtained from the same polymers. Peak resolution is good and qualitative identification is readily made. It was shown, with the use of FT-IR/PAS, that Estane 5703® and Phenoxy PKHH® were adsorbed from solution by *gamma*-iron oxide, but that Phenoxy PKHH® is preferentially adsorbed over the Estane 5703®.

TABLE II. **Ratio of peak heights of the urethane amide II carbonyl at 1530 cm^{-1} to the Phenoxy® aromatic stretch at 1510 cm^{-1}.**

Sample	Ratio
Without oxide	1.2:1.0
With oxide	0.5:1.0

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1. H. F. Huisman, H. J. M. Pigmans, A. J. P. Roegies, and W. J. J. M. Sprangers, Prog. Org. Coatings **13**, 377 (1986).
2. D. J. Gerson, Appl. Spectrosc., **38**, 436 (1984).
3. J. L. Koenig, *Fourier Transform Spectroscopy of Polymers*, Advances in Polymer Science 54 (Springer-Verlag, Berlin/ Heidelburg/ New York/Tokyo, 1983), p. 87.
4. Y. S. Lipatov, T. T. Todosijchuk, V. N. Chornaya, and T. S. Khramova, J. Coll. Interface Sci. **110**, 1 (1986).
5. Y. S. Lipatov, L. M. Serfesva, T. T. Todosijchuk, and V. M. Chornaya, J. Coll. Interface Sci. **86**, 437 (1982).

The Seagull®: A Multifunctional Variable-Angle Reflection Attachment

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Index Headings: **Variable-angle reflection spectroscopy; Instrumentation; Spectroscopic techniques.**

INTRODUCTION

Variable-angle reflectance is an important spectroscopic technique. Certain samples such as opaque substances, films on opaque substrates, and films on liquids are tedious or practically impossible to analyze via conventional transmission spectroscopy equipment. The analyses of such samples by reflection spectroscopy, however, are straightforward.

There are three different methods of reflection spectroscopy, namely internal, external, and diffuse reflectance. The technique employed depends on the nature of the sample and the information sought. External reflection spectroscopy is applicable to thin films on opaque substrates and opaque smooth solids. Internal reflec-

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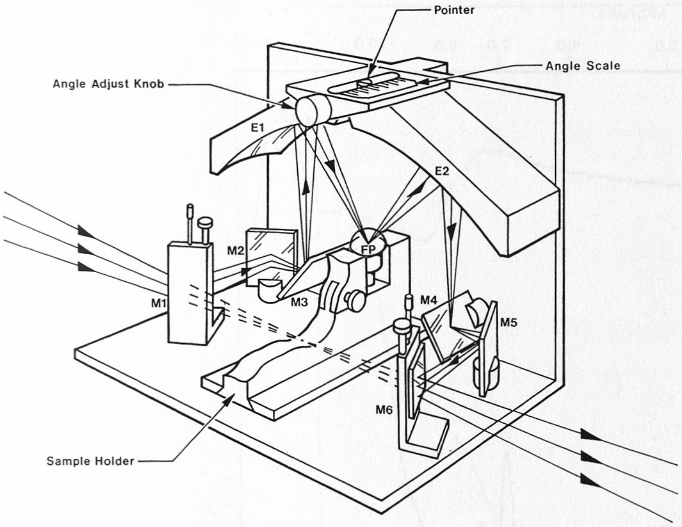

FIG. 1A. The Seagull® variable-angle reflection accessory.

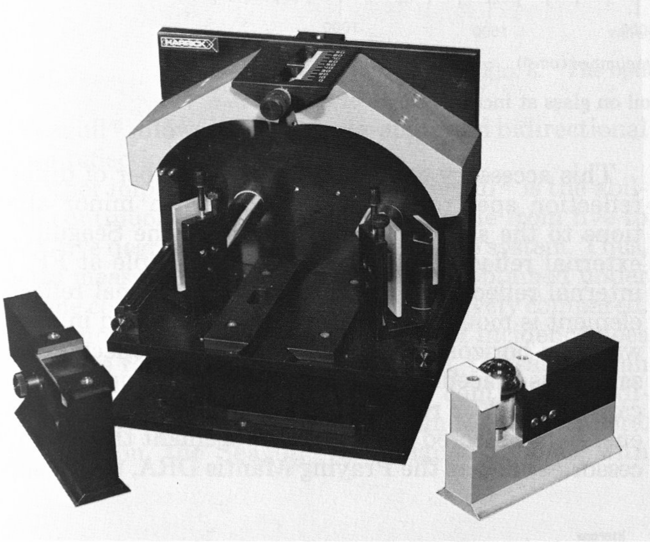

FIG. 1B. Photograph of the Seagull® variable-angle reflection accessory.

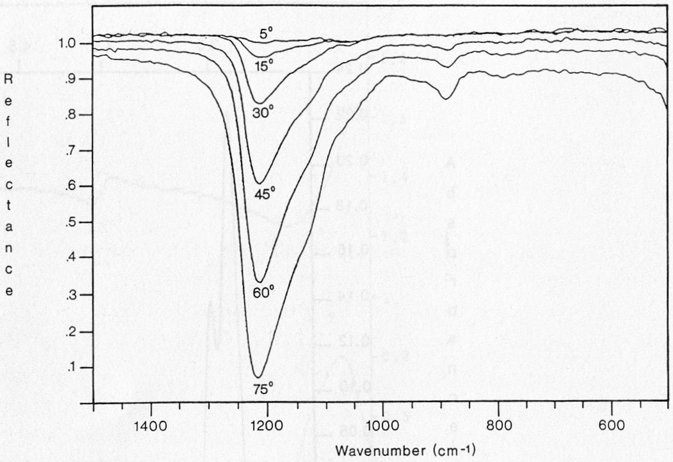

FIG. 2. External reflection spectra of 0.05-μm SiO_2 film on aluminum (*p* polarization).

tance permits spectral measurements of liquids, powders, pastes, gels, and soft solids. Diffuse reflectance is most commonly used for the analysis of powders and rough surface solids.† Variable-angle studies, using either external or internal reflection spectroscopy, provide data for the determination of optical constants and sample thicknesses.

The spectrometer accessories currently available generally perform only one of the three reflection techniques, and the available variable-angle accessories have certain limitations imposed by their design. In particular, the variable-angle external reflection accessories, like the VRA with RMA,[1] probe different areas of the sample and defocus the beam on the sample as the incident angle changes. For variable-angle internal reflection accessories, such as the TMP,[2] the alignment of the accessory must be changed when a different incident angle is desired. Furthermore, for the examination of a large range of incident angles with the TMP, the internal reflection element must also be changed, which requires reapplying the sample and introduces the problem of reproducible sample/IRE contact. These restrictions make variable-angle studies unnecessarily complicated.

The Seagull®,‡ the new reflection accessory described here, overcomes these design limitations and can be adapted for all three reflection techniques.

EXPERIMENTAL

The design of the variable-angle reflection accessory, the Seagull®, includes several advanced features which add to its utility and flexibility.

A schematic diagram and photograph of this accessory are shown in Figs. 1A and 1B. Two ellipsoidal mirror segments are arranged with a common focal point (FP), as shown in Fig. 1A. The incoming beam is directed by mirrors M1 and M2 to mirror M3. The light focused on

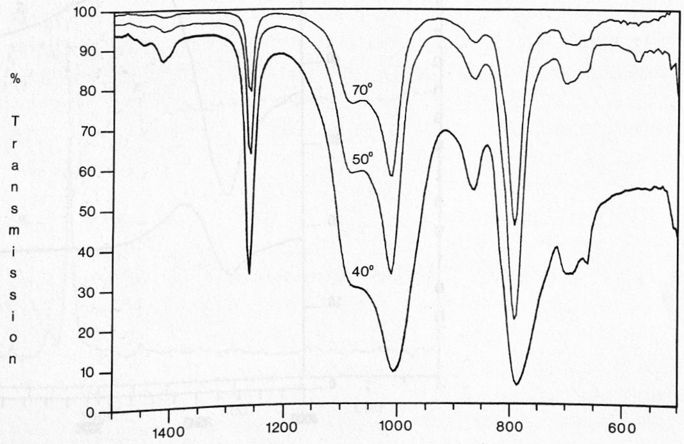

FIG. 3. Internal reflection spectra of silicone rubber.

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† Spectra of solid and liquid samples with smooth surfaces can also be recorded via diffuse reflection in the transflectance mode where a nonabsorbing material with one rough surface is placed in contact with the sample. The rough surface scatters the incident and reflected radiation, and a diffuse reflection spectrum is obtained.

‡ Patent pending.

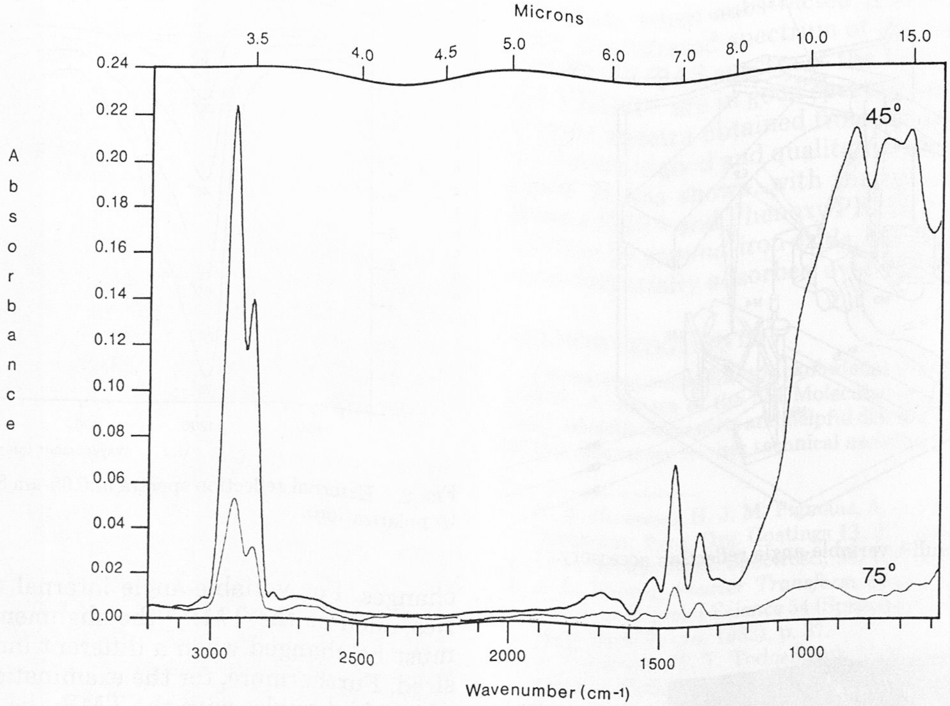

FIG. 4. Internal reflection spectra of paraffin oil on glass at incident angles of 45 and 75°.

mirror M3 can be directed to various areas of the first ellipsoid, E1. This ellipsoid refocuses the beam on the sampling plane, FP. As the beam sweeps left to right on E1, the angle of incidence on the sample decreases from approximately 85 to 5°. The second ellipsoid, E2, collects the radiation reflected from the sample and redirects it to mirror M4. Mirror M4 directs this radiation to mirrors M5 and M6 and then onto the detector. Mirrors M3 and M4 are coupled to rotate together, in mirror image fashion, when the angle of incidence is changed. This preserves the optical alignment for all incident angles.

This accessory can be used for a number of different reflection spectroscopy techniques with minor alterations to the sample holder. To adapt the Seagull® for external reflectance, one places the sample at FP. For internal reflectance, a hemispherical internal reflection element is mounted at FP directly above and in contact with the horizontal sample. For diffuse reflectance, the sample is placed at FP in or on a sampling cup which can be tilted or rotated. Although less of the reflected energy is collected with this arrangement than with accessories such as the Praying Mantis DRA, the design of

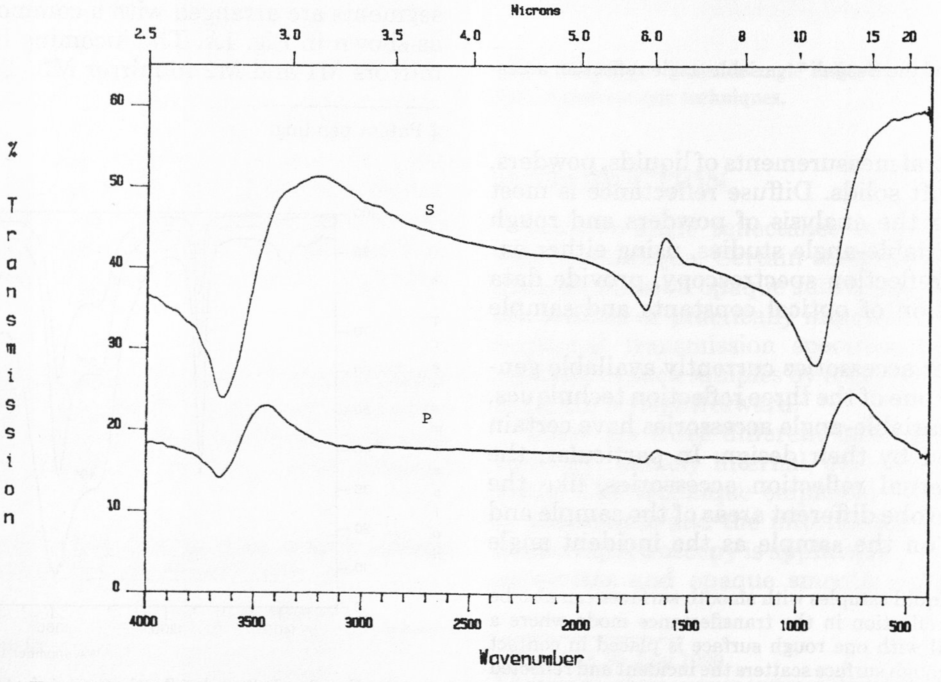

FIG. 5. External reflection spectra of the surface of water at an incident angle of 75° (*s* and *p* polarizations).

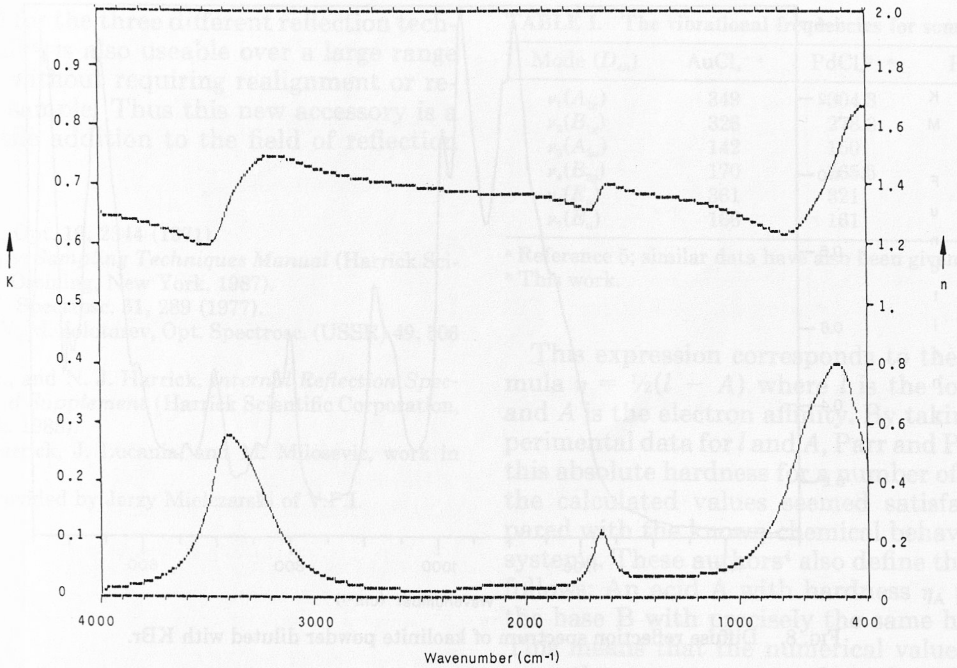

FIG. 6. The optical constants of water.

the Seagull® allows both variable-angle and bidirectional diffuse reflection measurements.

Another important feature of the Seagull® is the ability to continuously vary the incident angle from five to eighty-five degrees without misaligning the system. Thus, spectra measured at different angles are obtained under the same conditions and can be quantitatively compared. Furthermore, since changing the angle of incidence does not require repositioning of the sample, the sample can easily be enclosed in a chamber with controlled conditions, such as temperature, pressure, and/or atmosphere.

In addition, the Seagull® is designed so that, with changes in the incident angle, the focal point of the incident beam is always on the sample and reflects from the same area of the sample. This minimizes the required sample area and, since the focus is on the sample, permits examination of samples with a moderate curvature. Furthermore, areas of special interest, such as contaminants or surface defects, may be isolated for analysis.

A further feature of the Seagull® is that the polarization of the incident light does not vary with changes in the incident angle. This is essential, since reflectance depends on the polarization of the incident light. In order to compare the experimental measurements to the the-

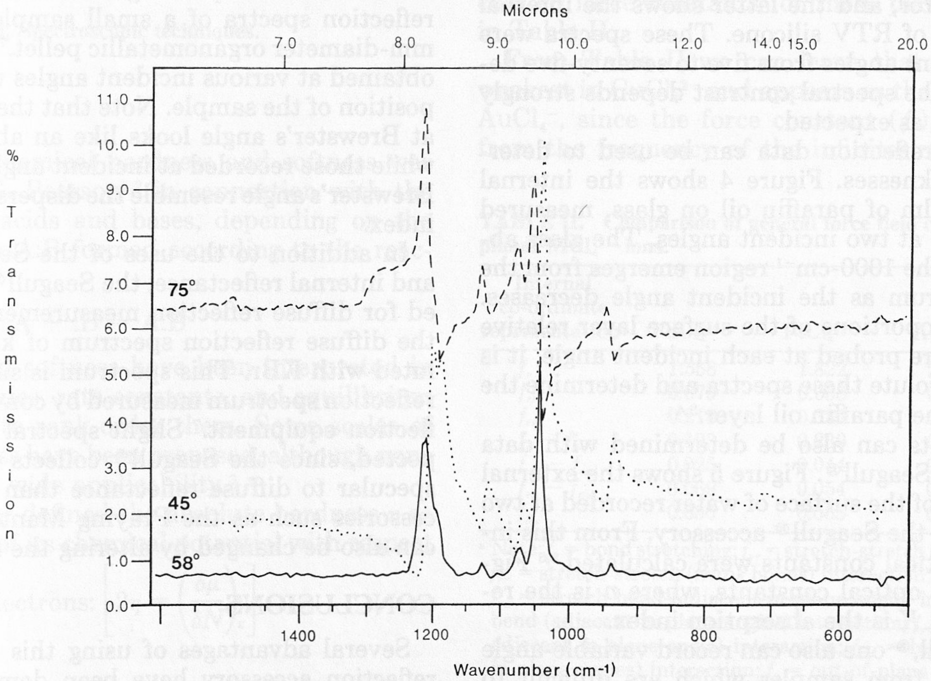

FIG. 7. External reflection spectra of a 0.5-in.-diameter organometallic pellet (*p* polarization at incident angles of 45, 58 and 75°).

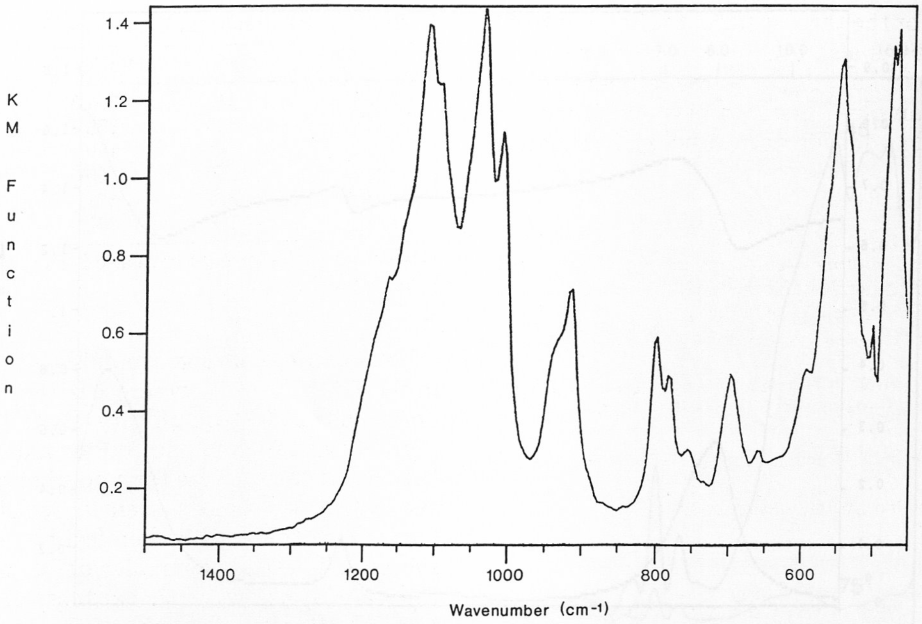

FIG. 8. Diffuse reflection spectrum of kaolinite powder diluted with KBr.

oretical expressions, the polarization of the incident light must be known.

RESULTS

Some applications of this new attachment are illustrated here. The results presented were obtained with the Seagull® in conjunction with a Mattson Sirius 100 FT-IR spectrophotometer. For the internal reflection studies, the internal reflection element was a ZnSe hemisphere with a radius of 12.5 mm.

The design of the Seagull® allows it to be operated over a broad range of incident angles, as illustrated by the spectra in Figs. 2 and 3. The former shows the external reflection spectra of a 0.05-μm-thick SiO_2 film on an aluminum mirror, and the latter shows the internal reflection spectra of RTV silicone. These spectra were recorded at incident angles from five to seventy-five degrees. Note that the spectral contrast depends strongly on incident angle, as expected.

Variable-angle reflection data can be used to determine sample thicknesses. Figure 4 shows the internal reflectance of a film of paraffin oil on glass, measured with the Seagull® at two incident angles. The glass absorption band in the 1000-cm^{-1} region emerges from the paraffin oil spectrum as the incident angle decreases. Since different proportions of the surface layer relative to the substrate are probed at each incident angle, it is possible to deconvolute these spectra and determine the depth profile of the paraffin oil layer.[3,4]

Optical constants can also be determined with data acquired with the Seagull®. Figure 5 shows the external reflection spectra of the surface of water recorded at two polarizations with the Seagull® accessory. From this information, the optical constants were calculated.[5,6] Figure 6 shows these optical constants, where n is the refractive index and K is the absorption index.

With the Seagull,® one also can record variable-angle reflection spectra from samples which are difficult to examine due to sample form or size. Liquid samples, for example, fall into this category since, in standard accessories such as the VRA with RMA, samples are normally mounted vertically. In the Seagull®, however, the sampling surface is horizontal. Figure 5, as mentioned previously, shows the spectra of liquid water obtained with the Seagull®. In addition to liquids, small samples pose problems in variable-angle reflectance. Traditional variable-angle reflection accessories, such as the VRA with RMA, do not probe the same area of the sample when the incident angle is varied. With small samples, recording spectra at various incident angles may require repositioning of the sample for different incident angles. The Seagull®, however, always centers the incident radiation on the same sample area, eliminating the need to move the sample. Figure 7 illustrates the external reflection spectra of a small sample, specifically a 12-mm-diameter organometallic pellet.[7] These spectra were obtained at various incident angles without altering the position of the sample. Note that the spectrum obtained at Brewster's angle looks like an absorption spectrum, while those recorded at incident angles above and below Brewster's angle resemble the dispersion in the refractive index.

In addition to the uses of the Seagull® for external and internal reflectance, the Seagull® can also be adapted for diffuse reflection measurements. Figure 8 shows the diffuse reflection spectrum of kaolinite powder diluted with KBr. This spectrum is similar to the diffuse reflection spectrum measured by conventional diffuse reflection equipment.[7] Slight spectral differences are expected, since the Seagull® collects a different ratio of specular to diffuse reflectance than is collected by accessories such as the Praying Mantis DRA. This ratio can also be changed by altering the incident angle.

CONCLUSIONS

Several advantages of using this new variable-angle reflection accessory have been demonstrated here. In particular, the Seagull® is a versatile accessory which is easily reconfigured for the three different reflection techniques. The Seagull® is also useable over a large range of incident angles without requiring realignment or repositioning of the sample. Thus this new accessory is a flexible and versatile addition to the field of reflection spectroscopy.

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1. N. J. Harrick, Appl. Opt. **10**, 2344 (1971).
2. *Optical Spectroscopy: Sampling Techniques Manual* (Harrick Scientific Corporation, Ossining, New York, 1987).
3. T. Hirschfeld, Appl. Spectrosc. **31**, 289 (1977).
4. N. N. Rozanov and V. M. Zolotarev, Opt. Spectrosc. (USSR) **49**, 506 (1980).
5. F. M. Mirabella, Jr., and N. J. Harrick, *Internal Reflection Spectroscopy: Review and Supplement* (Harrick Scientific Corporation, Ossining, New York, 1985).
6. S. Berets, N. J. Harrick, J. Lucania, and M. Milosevic, work in progress.
7. This sample was provided by Jerzy Mielczarski of V.P.I.

A Spectroscopic Method for the Determination of the Absolute Hardness of Soft Acids

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Index Headings: **Infrared; Spectroscopic techniques.**

INTRODUCTION

The concept of chemical hardness and softness was introduced by R. G. Pearson[1,2] in connection with the behavior of Lewis acids and bases, depending on the stability of complex A:B formed according to the reaction:

$$A + :B \rightarrow A:B$$

The hardness and softness have been interpreted in terms of bond energies, rate constants, and equilibrium constants in order to rank-order them. Some scales of hardness and softness have been proposed, although none of them have had a wide applicability.[3]

Parr and Pearson[4] defined the absolute hardness η as the half-derivative of its chemical potential with respect to the number of electrons: $\left[2\eta = \left(\frac{\delta\mu}{\delta N}\right)_z\right]$.

TABLE I. The vibrational frequencies for some planar MCl_4^{n-} ions.

Mode (D_{4h})	$AuCl_4^-$ [a]	$PdCl_4^{2-}$ [a]	$PtCl_4^{2-}$ [a]	$CuCl_4^{2-}$ [b]
$\nu_1(A_{1g})$	349	304.3	331.3	274
$\nu_2(B_{1g})$	326	278.3	311	200
$\nu_3(A_{2u})$	142	150	147	158
$\nu_4(B_{2g})$	170	165.5	164.5	180
$\nu_6(E_u)$	361	321	313	291
$\nu_7(E_u)$	166	161	165	185

[a] Reference 5; similar data have also been given by Goggin and Mink.[7]
[b] This work.

This expression corresponds to the approximate formula $\eta = \frac{1}{2}(l - A)$ where l is the ionization potential and A is the electron affinity. By taking appropriate experimental data for l and A, Parr and Pearson[4] calculated this absolute hardness for a number of simple chemicals; the calculated values seemed satisfactory when compared with the known chemical behavior of the selected systems. These authors[4] also define the HSAB theory as follows: An acid A with hardness η_A prefers to bind to the base B with precisely the same hardness ($\eta_B = \eta_A$). This means that the numerical values for acids should span the same range as the values for bases with the same precision. This requirement presents a practical problem since, for example, the η for Pt^{2+} could not be calculated, as the third ionization potential is not known.

In this work we present an alternative way to calculate the absolute hardness of soft metal ions by comparing the interaction force constants, calculated from a General Force Field.

DISCUSSION

We recently published a paper on the infrared and Raman study of the planar $CuCl_4^{2-}$ complex in $(LH)_2CuCl_4$ (LH = 2-aminobenzothiazole).[5] The vibrational frequencies of the planar $CuCl_4^{2-}$ group and some other planar MCl_4^{2-} ions[6,7] are summarized in Table I; the calculated force constants for these planar ions are given in Table II.

From Table II we can learn that the MCl bond is weakest in $CuCl_4^{2-}$ and appears as the strongest bond in $AuCl_4^-$, since the force constant (f_r), when calculated from the frequency of the infinitesimal vibration, is a

TABLE II. Comparison of general force field constants (10^2 nm^{-1}) for planar MCl_4^{n-} ions.

Internal co-ordinate representation[a]	$PdCl_4^{2-}$ [b]	$PtCl_4^{2-}$ [b]	$AuCl_4^-$ [b]	$CuCl_4^{2-}$ [c]
f_r	1.558	1.822	2.205	1.017
f_{rr}	0.079	0.068	0.081	0.183
$f_{rr'}$	0.218	0.334	0.177	0.185
$f_\alpha - f_{\alpha\alpha'}$	0.193	0.230	0.228	0.248
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.025	0.044	0.038	0.039
$f_{r\alpha} - f_{r'\alpha}$	0.069	0.054	0.054	0.073
f_β	0.050	0.065	0.061	0.160

[a] Note: f_r = bond stretching; f_{rr} = stretch-stretch (*cis* bonds) interaction; $f_{rr'}$ = stretch-stretch (*trans* bonds) interaction; f_α = in-plane bending; $f_{r\alpha}$ = stretch-bend (adjacent in-plane angle) interaction; $f_{\alpha\alpha}$ = bend-bend (adjacent in-plane angles) interaction; $f_{r'\alpha}$ = stretch-bend (nonadjacent in-plane angle) interaction; $f_{\alpha\alpha'}$ = bend-bend (nonadjacent in-plane angles) interaction; f_β = out-of-plane bending.
[b] Reference 7.
[c] This work.

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