

used, but the instrument does not function in the absence of a high concentration of hydronium ions.

The rapid explosion of hydrogen and oxygen causes emission of characteristic light which is dispersed by a reflexion grating. The spectra from the cations in the two cells are observed simultaneously through an eye piece on a scale graduated in Angstrom units. After an unknown ion has been detected, a known sample can be used in the reference cell for purposes of verification. The relative intensity of lines from the two cells can be used for semi-quantitative estimates.

The use of this instrument has been extended to the analysis of metals and other undissolved solids. Characteristic spectra are observed when filaments of metals or alloys are attached to the shorter electrode and immersed to a depth of about 1 mm in the acidified potassium nitrate solution.

Characteristic spectra of cations were also observed when 100 mg samples of finely divided solids were suspended in the test solution. Some salts dissolved to some extent during the test, but sharp spectral lines were also obtained for sparingly soluble solids. Thus, this versatile instrument may be used to detect a large number of cations as solids or in solution. Some of the solids tested directly were copper, steel, silver, nickel-chromium alloy, silver chloride, ferrous sulphide, barium sulphate, lead sulphate, bismuth hydroxide, strontium sulphate, chromic oxide, manganese dioxide, calcium oxide, aluminium oxide, arsenic oxide and stannic oxide.

These techniques, coupled with anion analysis by infra-red and ultra-violet spectroscopy, provide a new approach to rapid qualitative analysis.

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¹ U.S. patents 3,024,693 and 3,045,533 issued to Dr. Duane D. Harmon and assigned to Fisher Scientific Co.

Single and Multiple Reflexion Attenuated Total Reflectance Infra-red Spectroscopy

LEST the communication of Baxter and Puttnam¹, indicating superiority of multiple reflexion in applying attenuated total reflexion to infra-red spectroscopy, be interpreted too literally and applied too widely, at least one additional factor should be pointed out.

It is true that multiple reflexion increases absorption of the individual peaks, and thus may amplify weak absorption spectra when compared with single reflexion attenuated total reflexion curves. But the higher losses of energy of all incident wavelengths, chiefly as a result of scattering, associated with multiple reflexion tend to offset the former effect, and in some cases to obscure completely any intensification arising from multiple reflexion. This is particularly true when low resolution spectrophotometers are used.

I have found that the interplay of these two opposing factors renders impossible prediction of which approach—single reflexion or multiple reflexion—will serve best with a given sample. I usually try both techniques (as the time involved is not prohibitive) and then use whichever spectrum is better.

The infra-red curves shown in Fig. 1, which I have selected almost at random from spectra run in the past six months, illustrate my point. Both curves were run using a Perkin-Elmer Model 137 Infracord spectrophotometer. The single reflexion *ATR* unit used was the model *MATR*-1, manufactured by Connecticut Instrument Corporation (since acquired by Barnes Engineering). The multiple reflexion attachment was a Wilks Scientific Corporation model 9 with an *MIR*-2 sample holder, and using a 50 × 20 × 1 mm plate. Both attachments are single beam, and *KRS*-5 was used as the prism material in both cases. Other operating parameters were optimized

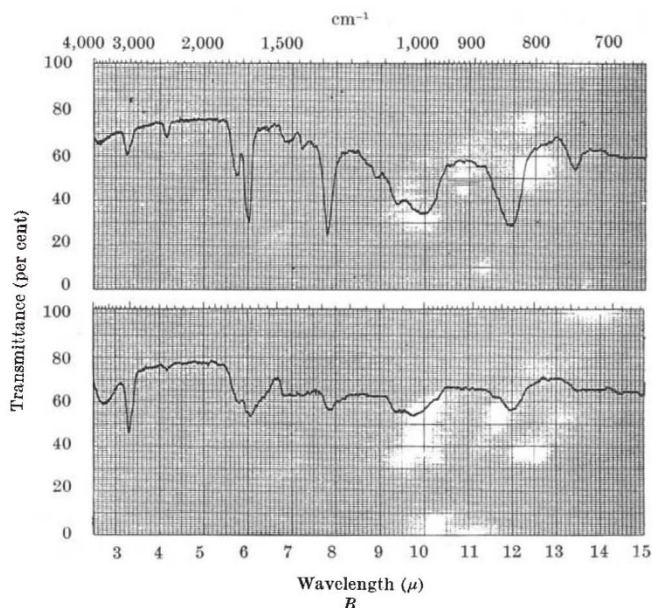


Fig. 1. Spectra of coated surface of coated aluminium foil. *A*, *ATR* unit; *KRS*-5 hemicylinder; slit 100; angle 52.5°. *B*, *FMR* unit; *KRS*-5 plate; slit 100.

separately for each sample in each attachment. With some samples the superiority of multiple reflexion is unquestioned.

Spectra *A* and *B* in Fig. 1 were run on the coated surface of a sample of coated aluminium foil. In this case the single reflexion (*A*) spectrum shows considerably more detail than does the multiple reflexion spectrum (*B*).

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¹ Baxter, B. H., and Puttnam, N. A., *Nature*, 207, 288 (1965).

Semiconductivity of Free Radicals of Nitric Oxide

ONE approach to the problem of producing highly conducting organic materials is to synthesize molecules with unpaired electrons which are capable of interacting to produce a half-filled band and thus exhibiting near-metallic behaviour¹. The free radicals examined so far do not show this behaviour²⁻⁵, mainly because their stability results from steric hindrance and electron delocalization which prevent both interaction and dimerization. In this connexion it is of interest to compare the radicals containing the N-O group, because in these the stability probably results largely from the nature of the N-O bonding.

The radicals studied were α,α -diphenyl- β -pieryloxy hydrazyl (DPPOH), di-*p*-anisyl nitric oxide (DANO), Banfield and Kenyon's radical (BK), di-*p*-nitrophenyl nitric oxide (DPNO). DPPOH was synthesized by the method of Poirier, Kahlen and Berrington⁶. Recrystallization from ethyl acetate gave dark green crystals with a melting point (m.p.) of 193°-196° C. DANO was synthesized by the method of Meyer⁷. Recrystallization from pyridine gave copper-bronze coloured needles with an m.p. of 120°-122° C. BK was synthesized by the method of Banfield and Kenyon⁸. The product was recrystallized from petroleum ether, giving maroon crystals with an m.p. of 80° C. DPNO was synthesized by the method of Wieland and Roth⁹. It separated from an ether-benzene mixture as a maroon powder with an m.p. of 109°-110° C. The electrical properties were measured using the techniques to be described elsewhere¹⁰.