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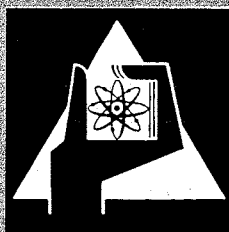
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An Experimental Contribution to the Measurement of
Optical Spectra by Scattered Transmission

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An Experimental Contribution to the Measurement of Optical Spectra by Scattered Transmission

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Teflon powder, compressed with the sample, is shown to have excellent properties for the measurement of spectra of polycrystalline actinide and lanthanide compounds by scattered transmission in the region from 350 to 2600 nm. In this way spectra can be obtained using samples which are extremely air and moisture sensitive. For example, the spectrum of pyrophoric *tris*-(cyclopentadienyl)-uranium (III) has now been measured for the first time. The resolution, especially in the ir region, is better than obtained by reflection methods, as is shown using ferrocene samples.

INDEX HEADINGS: Techniques, spectroscopic; Infrared, near; Visible, uv spectroscopy.

INTRODUCTION

The measurement of absorption spectra of sensitive substances, notably metallo-organic compounds in the visible and near ir region, presents experimental difficulties because no suitable solvent has been found. Either the substance is not soluble or it forms adducts with the solvent and in many cases the compound under study decomposes in the solvent used. Moreover, the intense combination vibrations and overtones often interfere. Thus no spectra can be obtained which represent the original molecules.

The following methods are usually employed to minimize these difficulties: (1) taking the spectra by diffuse reflection, (2) taking transmission spectra using a mull, and (3) taking transmission spectra of thin films.

Reid, Scaife, and Wailes¹ have used reflection methods for taking spectra of several cyclopentadienyl compounds. However, in addition to the poorer resolution afforded by these methods, the necessary pulverization is particularly bad with highly radioactive substances because of the danger of spreading contamination. For measuring spectra of hexanitrate actinides (VI) and hexahalolanthanide complexes in the visible region, Ryan and Jørgensen^{2,3} applied the mull technique, which is well known in ir spectroscopy.^{4,5} Here they used petrolatum or Kel-F (polytrifluoromonoethylen) as the matrix. However, very sensitive compounds such as $U(C_5H_5)_3$ and $Pu(C_5H_5)_3$ rapidly decompose in a Kel-F paste.

A thin sublimed film was used by Pappalardo, Carnall, and Fields⁶ for measuring the spectrum of *tris*-(cyclopentadienyl)-americium (III). This technique is, however, difficult to use, for in many cases the films so prepared were lost during simple evaporation because of the thermal sensitivity of the substance.

In attempts to take spectra of very sensitive compounds which decompose rapidly in Kel-F mulls, we found that disks compressed with Teflon were well suited for this purpose. In particular, they are suitable for measuring spectra of sensitive highly radioactive

substances at low temperatures, as well as normal temperatures. The technique is described below and the results of experimental measurements are given.

I. EXPERIMENTAL

The substance to be investigated was finely powdered⁷ and thoroughly mixed with Teflon powder (type BK3 obtained from C. Roth and Company, Karlsruhe) by the use of a sharp-bladed stirrer. The disks were compressed under a pressure of 5–15 tons using a

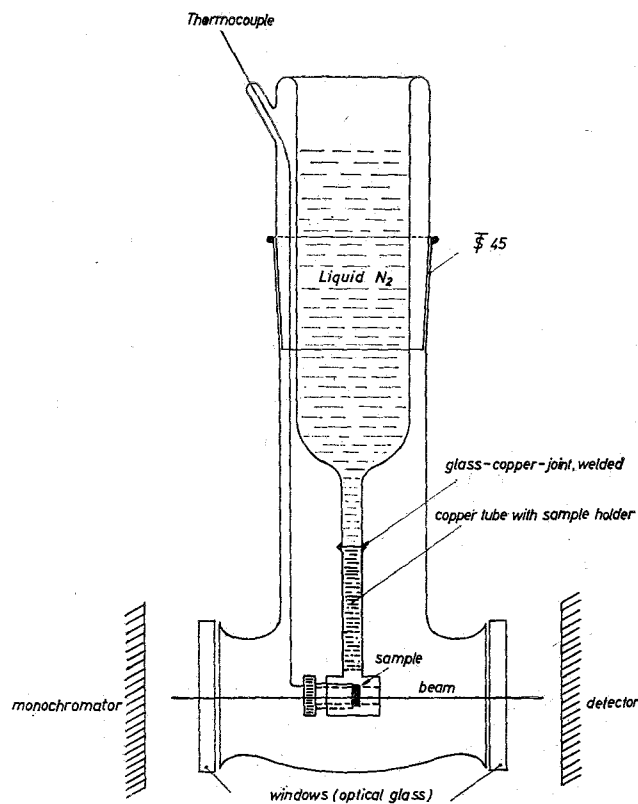


FIG. 1. Glass Dewar with copper welded joint to take spectra of Teflon disks at low temperatures.

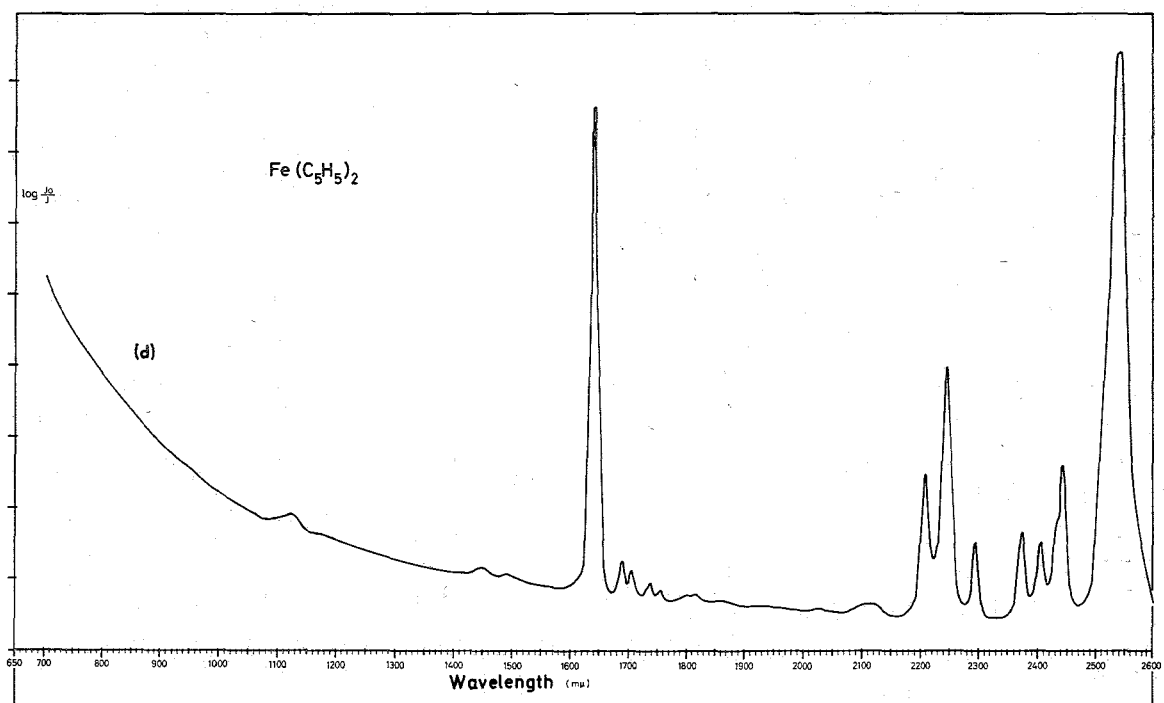
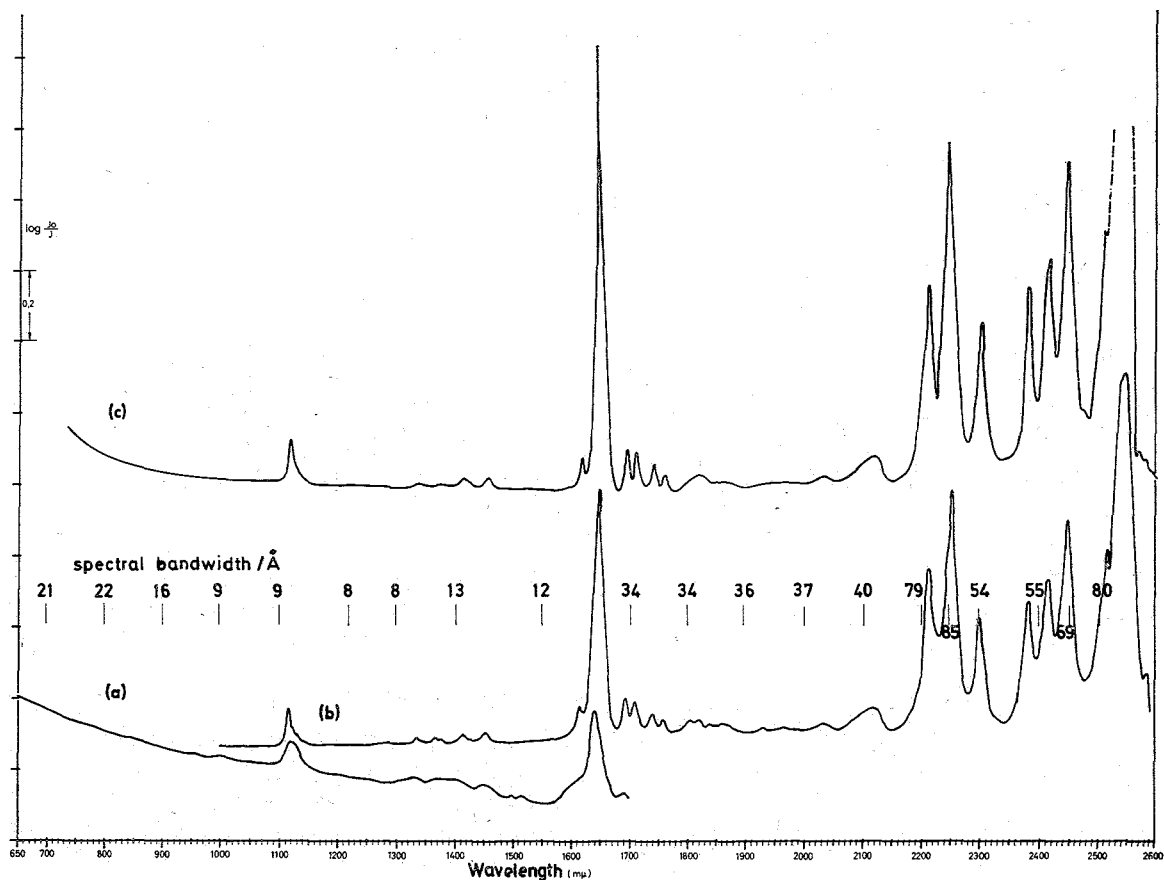
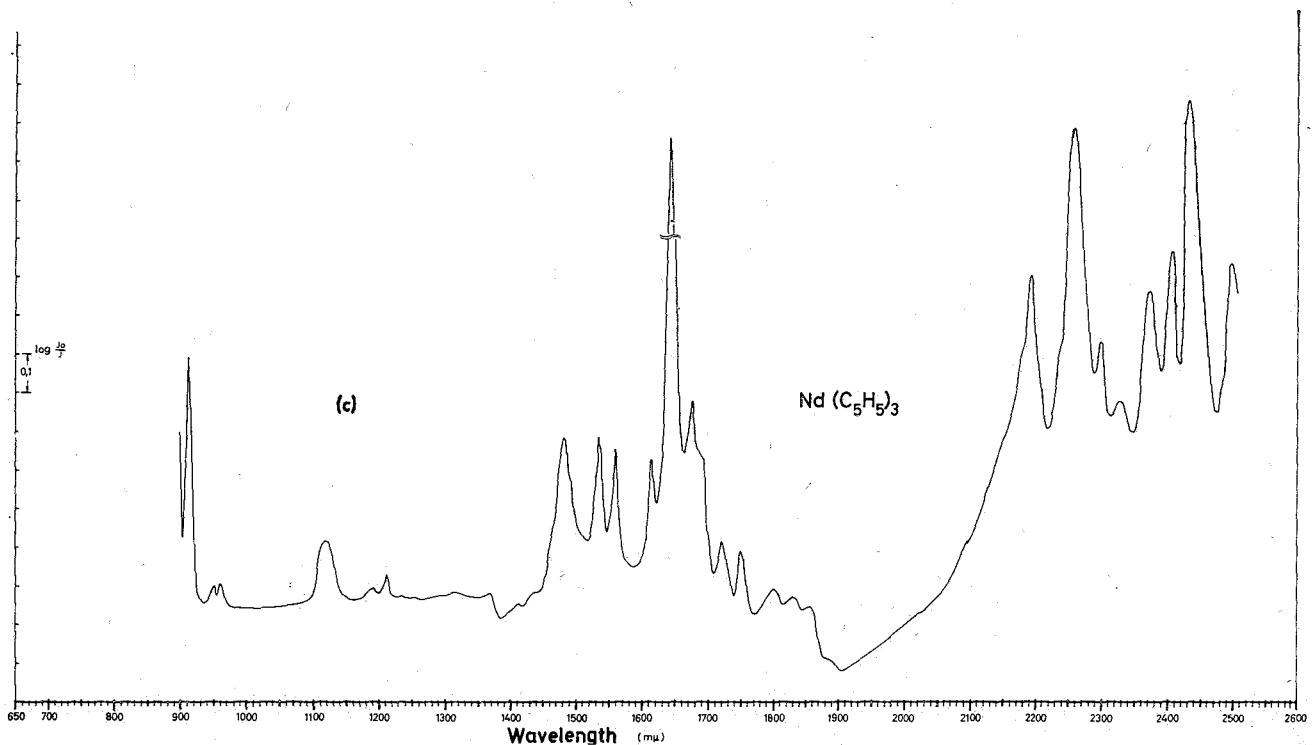
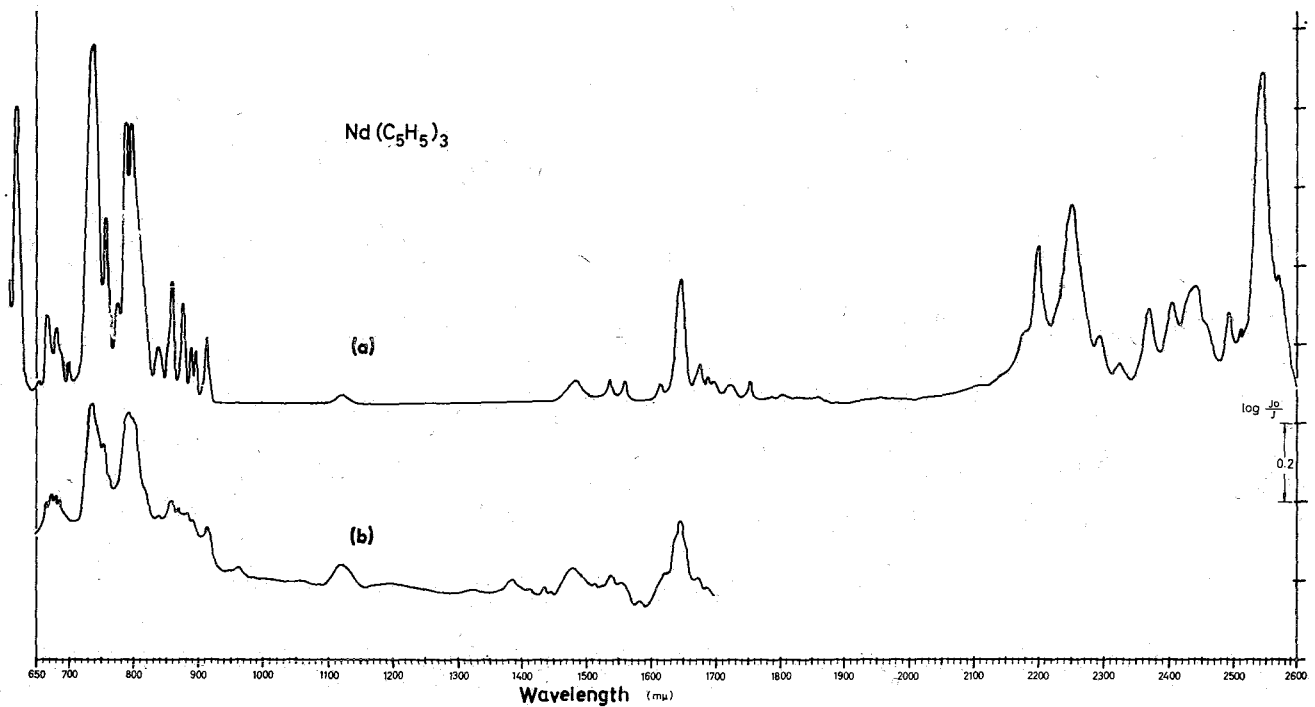


FIG. 2. Spectra of ferrocene at room temperature. (a) Reflection spectrum. (b) Teflon-disk, approximately 4 mmol ferrocene/g Teflon. Reference sample approximately 30 mg Al_2O_3 , 40 mg Teflon. Disk thickness 0.3 mm. Spectral bandwidths are given for some wavelengths. (c) Kel-F mull, approximately 5.5 mmol ferrocene/g Teflon. Reference sample approximately 0.3 g CaCO_3 /g Kel-F. Thickness ~ 0.15 mm. (d) CCl_4 Solution of ferrocene, 0.4 moles/liter, pathlength 1 cm.

hydraulic press (Perkin-Elmer Company, Bodensee). In the case of air sensitive substances, all weighing, mixing, and pressing were done under a protected atmosphere, using the usual Schlenk tube technique.⁸ The diameter of the disks obtained was 13 mm. (Good results were also obtained for ferrocene by using a pellet of only 2 mm diameter.) The disk thickness was varied between 0.25 and 0.45 mm for ferrocene. As a reference sample we used a disk of Teflon and finely powdered aluminum oxide. This

reference sample must be made to match closely the sample under study to compensate for the fraction of scattered light. The required aluminum oxide concentration and grain size for the reference samples were determined empirically. It is recommended that a range of such samples must be prepared with different aluminum oxide concentration so that the best choice can be made by experiment.

All spectra were taken with a Cary model 14 spectrophotometer. To keep the spectral bandwidth



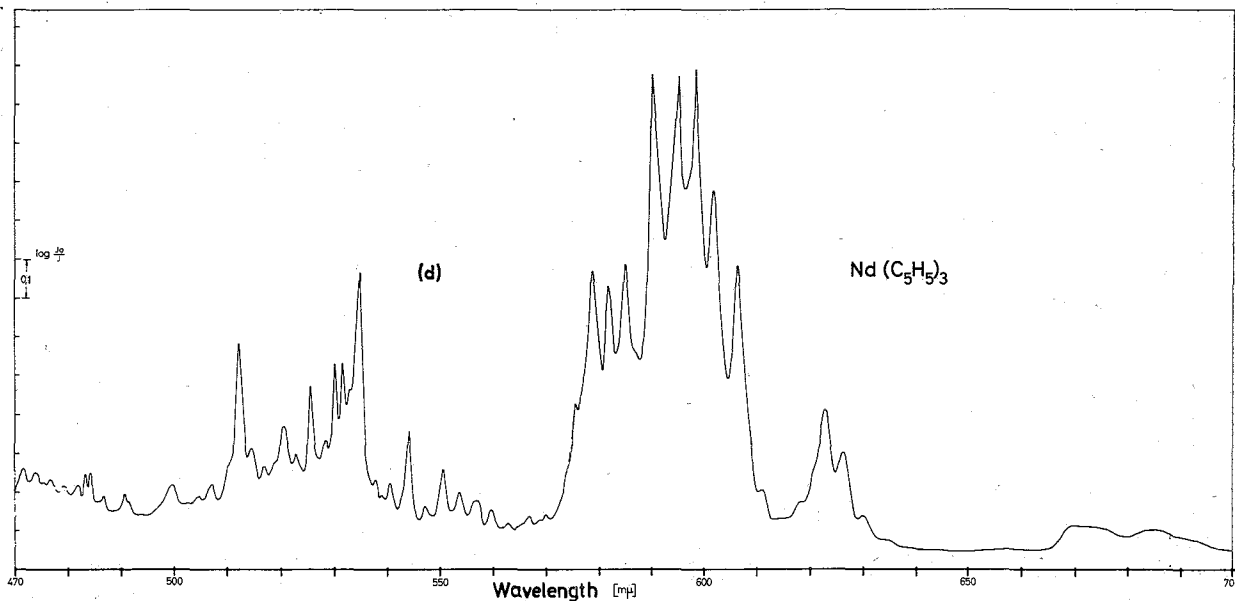


FIG. 3. Spectra of *tris*-(cyclopentadienyl)-neodymium(III) at room temperature. (a) Kel-F mull, concentration and thickness as Fig. 1; (b) reflection spectrum; (c) Teflon disk, approximately 7 mmol $\text{Nd}(\text{C}_5\text{H}_5)_3/\text{g}$ Teflon, thickness ~ 0.4 mm; (d) Teflon disk, 3 mmol $\text{Nd}(\text{C}_5\text{H}_5)_3/\text{g}$ Teflon, thickness approximately 0.15 mm.

as narrow as possible we worked mostly with high amplification and also used weakly scattering reference samples so that the spectra could all be recorded in

the extinction range between 1 and 2. A suitable cooling device Fig. 1 made the measuring of spectra at low temperatures very simple. The efficiency of

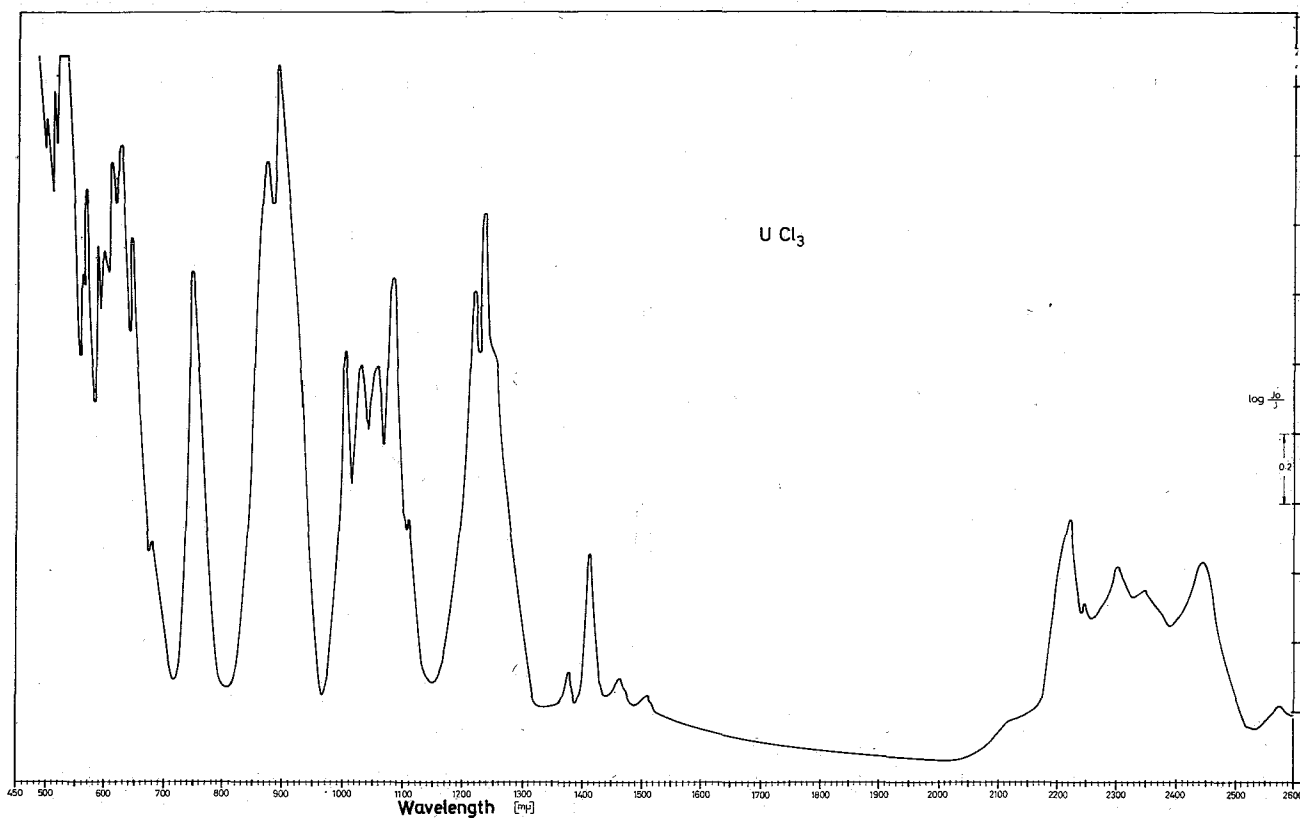


FIG. 4. Spectra of anhydrous uranium(III)-chloride at room temperature. Teflon disk, approximately 4-5 mmol UCl_3/g Teflon, thickness ~ 0.25 mm.

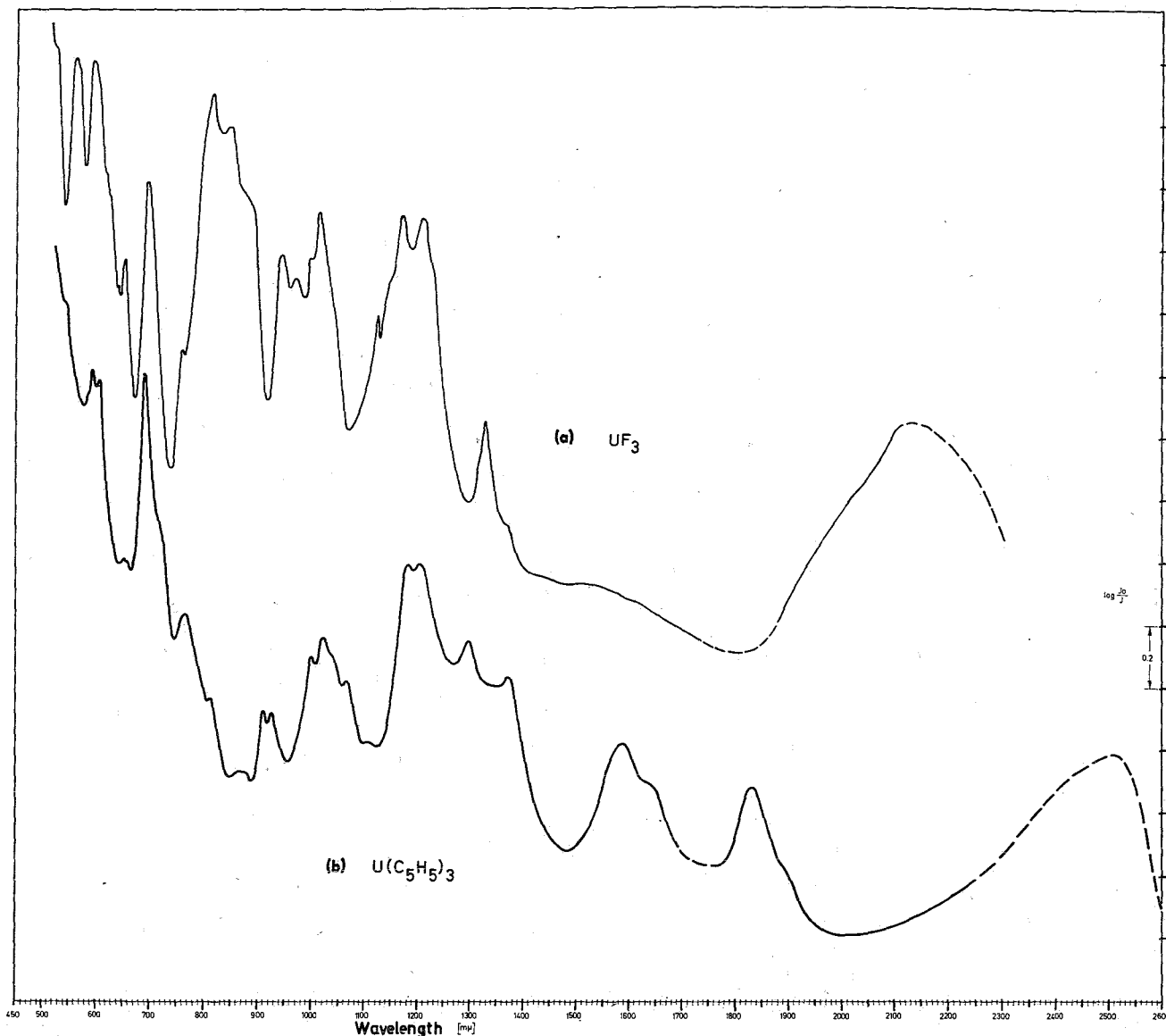


FIG. 5. Spectra from Teflon disks of uranium(III) compounds at room temperature. (a) Uranium(III)-fluoride; (b) *tris*-(cyclopentadienyl)-uranium(III).

light utilization, which is important in high resolution work, can be markedly improved by the use of a photometer sphere or a light pipe placed directly behind the sample. In the visible region, a corresponding improvement is certain to be attained through the use of the new scattered transmission accessory (Cary No. 1462).

An essential advantage of this method over the mull method is that practically all of the material to be studied actually is used in the measurement, while in the mull method significant amounts remain in the mixing vessel. Moreover, the sample thickness is easier to reproduce and measure.

Because of the good flow properties of Teflon powder under high pressure, the sample is subjected to an encapsulation effect whereby the decomposition of air sensitive substances is strongly inhibited.

II. RESULTS

Using the technique described, we have taken a large number of spectra of oxides, halides, metallo-organic compounds, and chelate complexes of the lanthanides and actinides with oxidation states III-VII. The spectra will themselves be described in greater detail in a subsequent publication, especially with respect to their theoretical interpretation. The capabilities of the method are compared with other techniques and are shown for a few representative substances in the following figures.

In Fig. 2 results of the various methods of taking spectra are compared using ferrocene as example. The spectrum shown in Fig. 2(a) was obtained using the simple Cary reflection attachment (model 1411750, direct radiation). It was not possible to reach higher

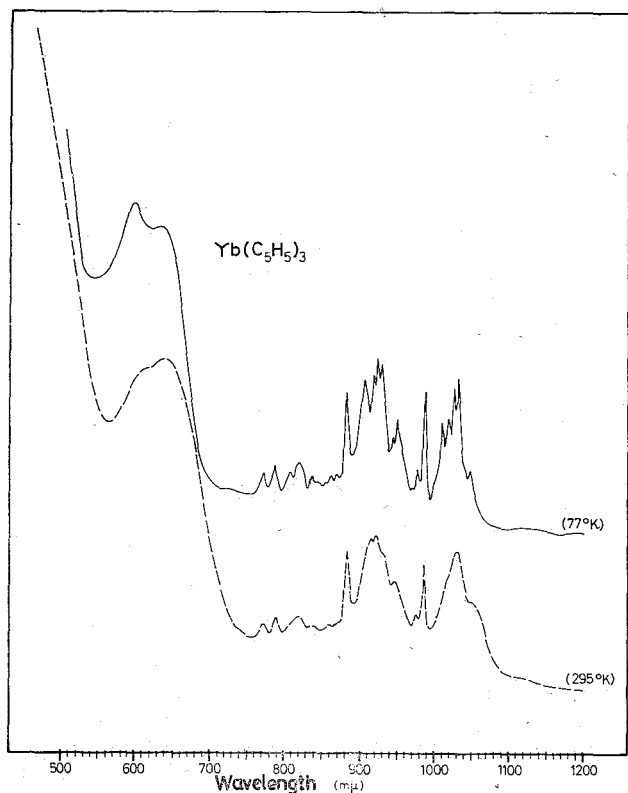


Fig. 6. Spectra of *tris*-(cyclopentadienyl)-ytterbium(III) at room temperature and 77 K, Teflon disk.

intensities. A spectrum of ferrocene in the near ir region taken with a nonrecording spectrophotometer, using a double monochromator (glass) and a reflection attachment, shows a strong shifting (65 nm) of the 2550 nm band toward the shorter wavelengths and a shifting (25 nm) of the 2250 nm band to the longer wavelengths, compared to the other spectra in Fig. 2. Moreover, poorer resolution was noted with the reflection measurements for the three bands near 2400 nm. The latter effect was also noticeable in reflection spectra published by Reid *et al.*¹ Figure 2(b) shows the spectrum which was obtained using the Teflon disk. To aid in assessing the resolution, approximate bandwidths are given for several wavelengths. Figures 2(c) and 2(d) show the spectra as obtained with the mull method and in carbon tetrachloride solution, respectively.

In Fig. 3 are shown spectra of *tris*-(cyclopentadienyl)-neodymium(III) which were obtained using the mull method, the Teflon disk, and the reflection technique. The good resolution afforded in the visible region by the pressed disk method is especially noticeable in Fig. 3(d).

In Fig. 4 is given the spectrum of anhydrous uranium(III) chloride taken with a disk, using 4–5 mmol UCl_3/g of Teflon. In most other cases this same concentration was also sufficient to attain an extinction value greater than 1 for the intense bands.

Good absorption spectra of uranium(III) compounds are not easily obtained because these sub-

stances are very air and moisture sensitive. A number of authors^{10–13} have already published spectra of uranium(III) chloride, although mostly in aqueous solution. In such solutions there exists the fundamental uncertainty regarding the presence of uranium(IV). Cohen and Carnall¹¹ have in large measure circumvented this difficulty in that they applied a reducing potential to a mercury cathode in the cuvette, and so attempted to prevent the formation of uranium(IV). Barnard, Bullock, and Larkworthy¹³ have measured the spectrum of $U_2(SO_4)_3 \cdot H_2O$ by diffuse reflection. This spectrum agrees with that given in Fig. 4 for the most important bands, although uranium(III) chloride shows considerably stronger band splitting in the near ir and in the visible region.

In Fig. 5(a) is shown the spectrum of uranium(III) fluoride and in Fig. 5(b) that of *tris*-(cyclopentadienyl)-uranium(III). The spectrum of pyrophoric $U(C_5H_5)_3$ ¹⁴ could be obtained only by the Teflon disk technique, since the substance rapidly decomposes in Kel-F. Examples of the application of the disk technique for obtaining spectra at low temperatures are given in the following figures. Figure 6 shows a section of the spectrum of *tris*-(cyclopentadienyl)-ytterbium(III) at room temperature and at 77 K. The bands occurring in the region between 750 and 1050 nm, which are attributed to *f-f* transitions,¹⁶ show at liquid nitrogen temperature a considerable splitting as well as the expected increase in intensity. The broad double band occurring at 600 nm (which is regarded as a charge transfer band) shows a clear change at 77 K. Still more apparent is the influence of temperature on the spectrum of *tris*-(cyclopentadienyl)-uranium(IV)-fluoride, as is shown in Fig. 7.

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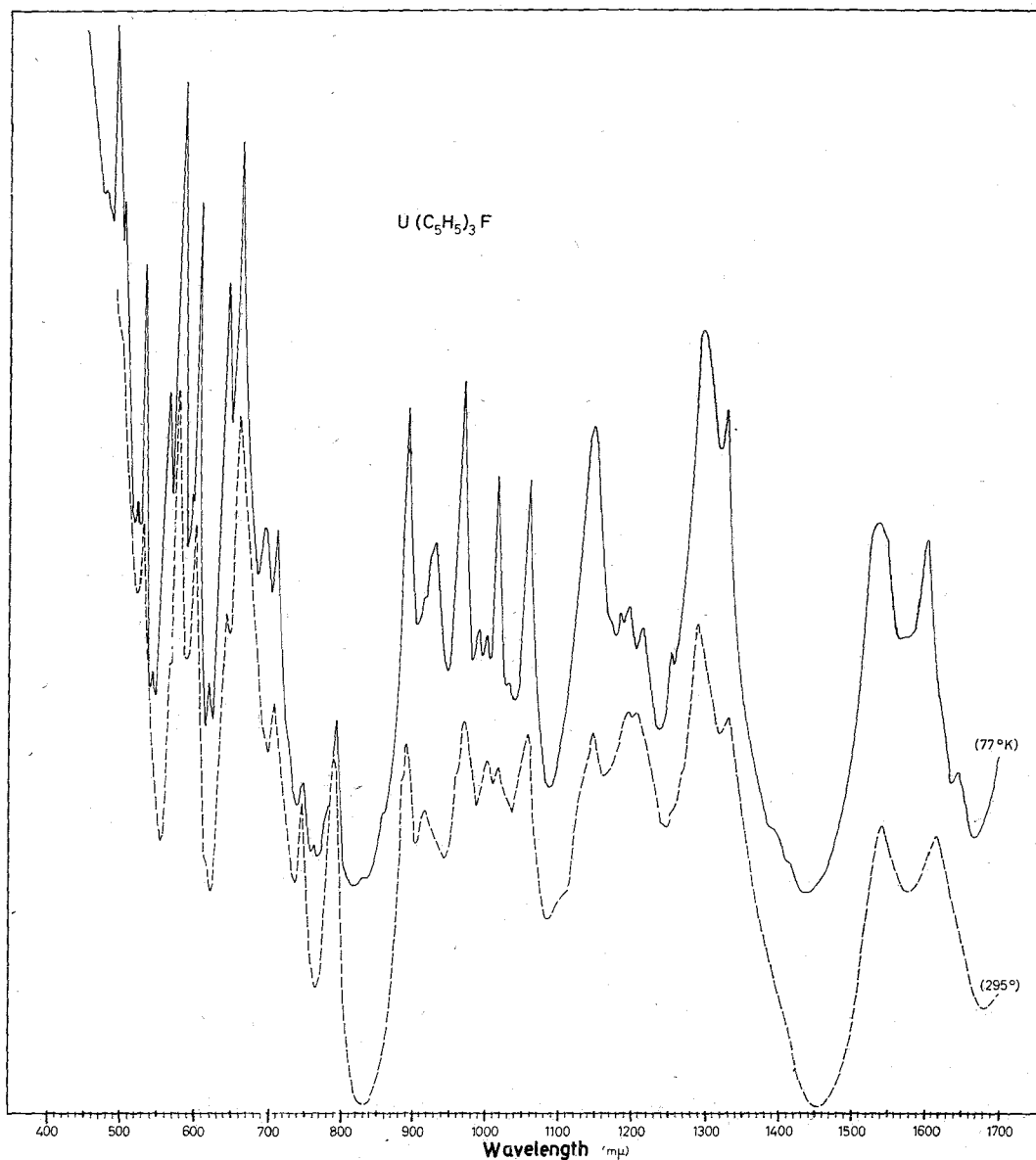


Fig. 7. Spectra of *tris*-(cyclopentadienyl)-uranium(IV)-fluoride at room temperature and 77 K, Teflon disk.

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