Teflon powders for near infrared spectra of hydrides

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Table III. Example of Nearest Neighbor Library
Searching Based upon Statistics Code

Unknown ($C_6H_{14}O$)
  Mean = 50
  Standard deviation = 17
  Skewness = 0.3
  Kurtosis = 220

The 5 nearest neighbors are:

	Mismatch index	Mean	Std dev	Skewness	Kurtosis
$C_6H_{14}O$	0.04	49.5	17.0	0.26	220
$C_7H_{16}O$	0.09	50.3	17.9	0.26	188
$C_8H_{18}O$	0.14	51.6	17.8	0.41	214
$C_8H_{18}O$	0.18	53.1	18.4	0.40	212
$C_7H_{16}O$	0.18	47.3	15.6	0.37	258

unknown was retained in its 32-bit format. With the library spectra also in 32-bit form, the unknown was still listed as one of the first 5 nearest neighbors, illustrating that entire 32-bit coding (library and unknowns) should generally be useful in library searching procedures of this type. The performance of the search routine was still creditable when further larger errors were introduced into the unknown. For example, when the standard deviation of $C_6H_{14}O$ was altered by 15% and the kurtosis by 10%, the correct compound was cited as the second nearest neighbor. It is also worth noting that, when weighting factors were not used, the correct compound was suggested as the third most likely neighbor. Finally, library searching using the statistics code performs well in terms of delineation from isomers and homologues. In some cases where the first neighbor listed was not the correct compound, the unknown was in the top two or three; the compounds ranked higher were almost always its isomers, with extremely similar mismatch indices. While one-bit encoding is generally not successful in separating isomers (1), the code used in this investigation was found to have a high success rate in doing so. Thirty-seven of the forty compounds used as unknowns were correctly listed as the first neighbor, even though isomers existed in the library.

CONCLUSIONS

In devising coding techniques to reduce redundancy, it is important to ensure that the essential information of a spectrum is not lost—i.e., it is important that the degree of uniqueness of encoded spectra be similar to that of full spectra. Certainly the results of this study imply that little spectral information is sacrificed in the coding method used even though the ultimate code length is only 32 bits. An accompanying advantage in choosing moments or moment-derived statistics is that errors in the determination of peak intensities will not be amplified in the code. Rather the accuracy of the moments will be of comparable order to that of the spectrum. On the other hand, errors in peak position could propagate larger moment errors, for which reason the technique is more suited to low resolution spectra in which all peaks are constrained to occur at integral mass numbers.

Clearly other codes based upon spectral statistics could be invented. For example it is possible to construct a reliable code based upon just mean and kurtosis, resulting in a greatly reduced code word length (20 bits) with reasonable discrimination ($\sim$1%). However the accuracy required in each of those parameters requires peak height precisions which are not practicable. Allocation of 8 bits to each of the four statistics is a compromise which does not place undue demands on the performance of a mass spectrometer and yet which yields very satisfactory results.

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Teflon Powders for Near Infrared Spectra of Hydrides

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Obtaining spectra in the near infrared region (1 μm to 3.5 μm) is usually difficult because of interference from water (OH stretch). One resorts to potassium bromide pellet with protective windows or heavy water solutions under very dry conditions. We would like to report here the use of Teflon (DuPont) as a pressable matrix, for the spectra in this region.

Teflon powders have been used for making strongly water repelling electrodes with great integrity and mechanical stability (1). These powders are now available commercially, and they can be used very easily for mixing and molding. We used both Teflon 7A and 7C, obtained from E. I. du Pont de Nemours and Company, Wilmington, Del., in our experiments.

The spectra were run on Beckman Acta IV and Perkin-Elmer Model 337. The pellets were made by weighing 100 mg of Teflon and pressing in a dye of $^3/_8$-inch diameter at a pressure of 12 tons, under vacuum. In Figure 1(a), the background spectrum of a pellet is shown. One could see that the material is transparent in the near IR region, with increasing scattering as the wavelength decreased.

In Figures 1(b) and 1(c) are shown the spectra of lithium aluminum hydride and sodium cyanoborohydride with the pellets made with very small quantities of each. The metal–hydrogen stretch (2) is dominant over the background. The stability of the pellets to moisture was clearly demonstrated
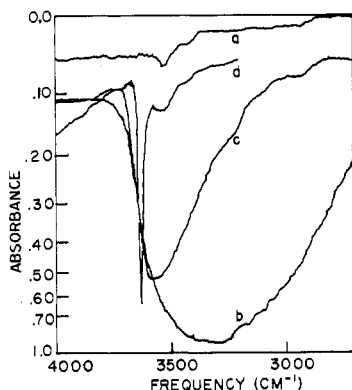
Figure 1. Infrared Spectra of Teflon pellets of various compositions. (a) Background spectrum of pellet. (b) Spectrum of lithium aluminum hydride in Teflon. (c) Spectrum of sodium cyanoborohydride in Teflon. (d) Spectrum of calcium hydroxide in Teflon

by the fact that when the pellet containing $LiAlH_4$ was placed in distilled water, except for very small initial bubbling on the surface, the pellet stayed intact. The spectrum shown in Figure 1(b) was exactly reproduced. The broadening of the spectra may be due to trace moisture entering the system prior to pressing, with water molecules coordinating to the metal. For reference we have shown the spectrum of $Ca(OH)_2$ in Teflon to locate the OH stretch.

We believe that this approach is a valuable analytical aid for the analysis of hydrides. With the future moving toward hydrogen storage, analysis of the hydride will play an important role. Further, obtaining near IR spectra of intervalence charge-transfer complexes is easier with Teflon than with D_2O.

ACKNOWLEDGMENT

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Modification of Pulse Polarograph for Rapid Scanning and Its Use with Stationary Electrodes

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Since its introduction by Parry and Osteryoung (*1, 2*), differential pulse polarography (DPP) at the dropping mercury electrode (DME) has become a widely employed technique for trace analysis of ionic and molecular species at concentrations of about 1 part per million and higher (*3–6*). On the other hand, differential pulse voltammetry (DPV) at stationary electrodes has until very recently been largely overlooked.

Christian (*7*) first reported that DPV at the hanging mercury drop electrode (HMDE) showed current behavior similar to that reported by Parry and Osteryoung for DPP at the DME. Keller and Osteryoung have derived equations for DPV at stationary electrodes for both reversible and irreversible systems (*8*), and Rifkin and Evans have published equations for reversible systems which include the effects of prior pulses on the concentration of the electroactive species in the diffusion layer (*9, 10*). Rifkin and Evans also demonstrated the analytical utility of DPV at platinum electrodes for analysis of sub-part per million concentrations of organic compounds. In both cases where theoretical equations were presented, the authors assumed a computer generated excitation function which is different from that generated by commercially available instrumentation.

Blutstein and Bond (*11*) have applied a rapid sweep differential pulse function to the DME. They utilized a commercially available polarographic analyzer whose circuit was modified to generate shorter pulse intervals and more rapid current response than are normally available on the instrument. While good sensitivity was obtained, the increase in the electrode area during the course of the experiment made a considerable contribution to dc faradaic and double-layer capacitance background currents, and distorted baselines became a significant problem at low analyte concentrations.

The principal practical advantage of DPV at stationary electrodes is that much shorter pulse intervals (time between successive pulse applications) may be employed, since the pulse intervals are no longer tied to the drop time of a DME. The use of shorter pulse intervals produces currents that are higher than those obtainable at the DME, and at the same time permits the use of much higher scan rates than can be used at the DME.

We are reporting here a set of simple and inexpensive modifications which can be made on a commercially available instrument to realize the enhanced analytical capabilities of DPV at stationary electrodes. The instrument is evaluated for the measurement of several metal ions at the HMDE; using the current readout of the instrument with no special data processing, accurate determinations are possible in the 25-ppb range, and detection limits of a few ppb are indicated. The voltammetric behavior of reversible and irreversible systems (in the dc polarographic sense) is briefly compared and the results indicate that the method may also be useful in the study of electrode kinetics. Dillard and Hanck (*12*) have recently reported on the application of DPP at the DME to the measurement of electrode kinetic parameters.

EXPERIMENTAL

A Princeton Applied Research Corporation Model 174 Polarographic Analyzer was modified as shown in Figure 1. The modifications made pulse intervals ("drop times") of 0.1 and 0.2 s available in addition to the normal 0.5, 1, 2, and 5-s intervals and also reduced the time constant of the current processing and readout circuitry from a measured value of about 500 ms to about 5 ms. A more complex time constant modification for the PARC 174 has recently been described by Abel et al. (*13*).