

Applications of Computer Difference Spectroscopy in Ion-Exchange Resins Analysis

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SYNOPSIS

Infrared spectra demonstrate the use of computer difference spectroscopy and other data-processing routines to derive and enhance the difference spectra that relates the concentration of a resin to the concentration of other resins in the mixture. Therefore, a simple quantitative treatment accounting for the resin concentrations has been determined.

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INTRODUCTION

Most resins used in water-purification applications are based upon polymers made from polystyrene and divinylbenzene. The reactive groups are usually attached to the aromatic rings in the chains and can be introduced before or after the resin has been formed. In nuclear systems, including waste treatment and water makeup, mixed bed units of strongly acidic cation and strongly basic anion exchangers are usually employed, for such mixtures remove the greatest variety of ions in the lowest concentrations and, hence, yield the highest purity water when used in the hydrogen and hydroxyl forms.

In the type of nuclear system application that we are discussing, it is desirable to regenerate the resin as completely as possible so as to obtain the greatest potential capacity and minimum leakage through the bed, compatible with the equivalent ratio of anionic and cationic resins. Among spectroscopic techniques, infrared (IR) is particularly useful for monitoring this ratio, and from the ratio of the absorbances, one may also measure the percentage present in a particular sample. Contained within this report is a description of the technique used for the computer subtraction of two resin mixtures in order to obtain the infrared spectrum of a single component. In this study, two resins made

from polystyrene and divinylbenzene (cross-linking agent) with different functional groups [RSO_3H , $\text{RCH}_2\text{N}(\text{CH}_3)_3^+ \text{OH}^-$] were evaluated using a small difference between the structures related. For this study, the most important bands are the vibration bands at about 830 cm^{-1} due to the vibrations of the cationic resin (C) and at about 825 cm^{-1} due to the vibrations of the anionic resin (A). Moreover, when the resins were mixed (M), the sample exhibited a shift of the peaks at about 827 cm^{-1} . In all spectra, this peak is observed at this position. Therefore, the IR absorption band at 827 cm^{-1} could be advantageously used for a given determination purpose. Physical mixtures of both resins of known composition (1 : 1) were required to ensure reproducibility of analysis.

EXPERIMENTAL

Characteristics of strongly basic anion and strongly acidic cation exchangers were of nuclear-grade Amberlite ion-exchange resins: cation-IRN-77 and anion-IRN-78. A mixture of both resins carefully weighted (1 : 1) was designated as M (Fig. 1). Also, the characteristics of both resins were examined individually, designed as A (anionic, Fig. 2) and C (cationic, Fig. 3), and the correlation among these two independent data were investigated. On the other hand, the characteristics of these resins used and decontaminated of the high radioactivity often present without chemical regeneration, designated

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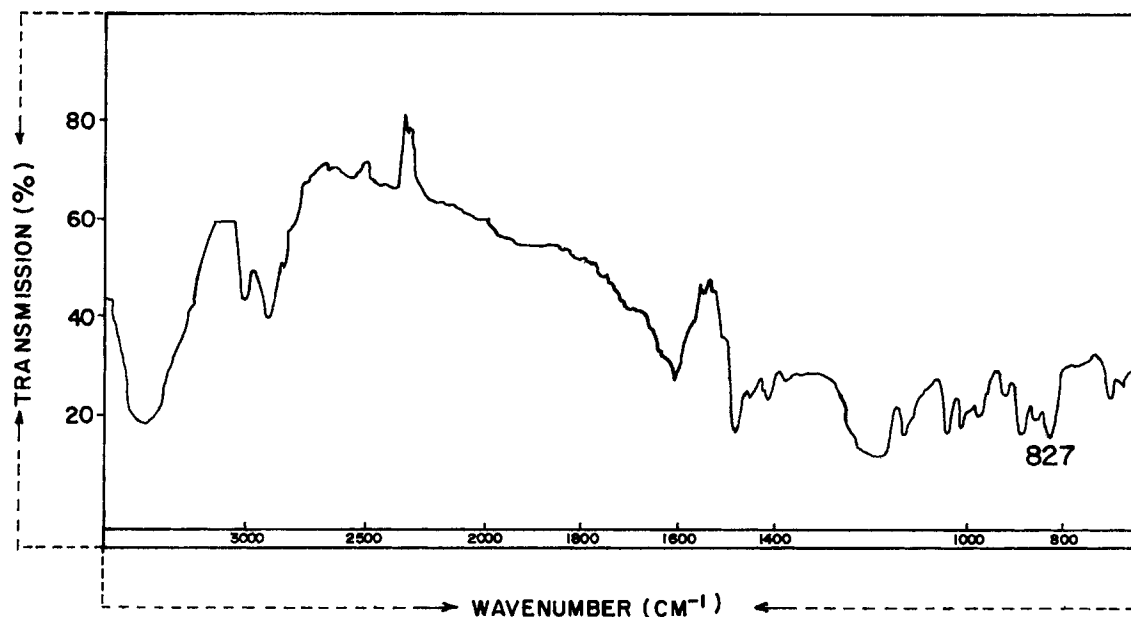


Figure 1 Infrared spectrum of the mixture of strongly basic anion IRN-78 and strongly acidic cation IRN-77 exchangers in proportion 1 : 1.

as *DM*, and after regeneration procedures, designated as *DRM*, were evaluated.

A mixture of both resins was prepared by weighing out equal amounts and then they were mixed thoroughly. Three milligrams of the mixture was then placed into a amalgamador with potassium

bromide (KBr), until 300 mg of the KBr was added and ground to reduce the particle size for 5 min of grinding time. The sample mixture was then pressed into a 9-mm-diameter KBr pellet. The sample was scanned from 4000 to 400 cm^{-1} using a wide slit program and a scan time of approximately 6 min at

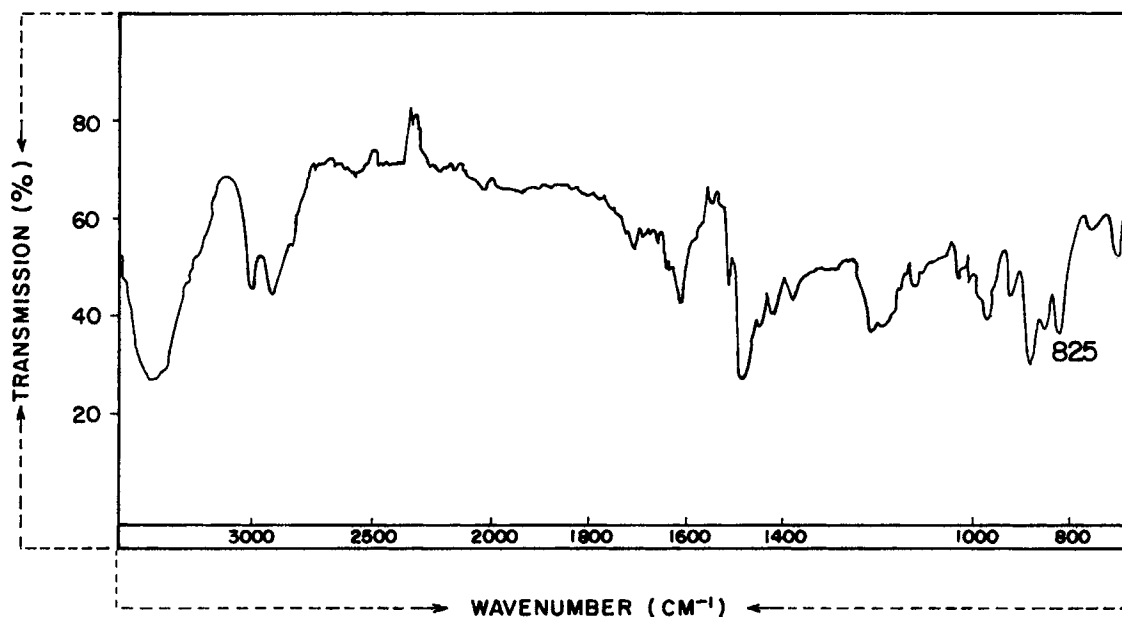


Figure 2 Infrared spectrum of the strongly basic anion IRN-78 resin.

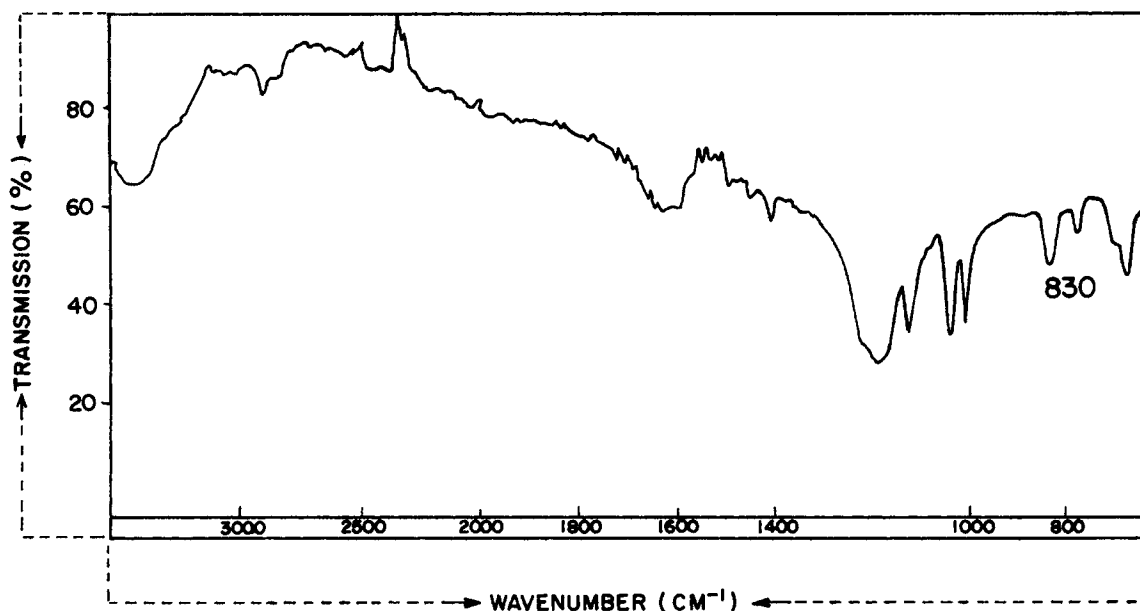


Figure 3 Infrared spectrum of the strongly acidic cation IRN-77 resin.

room temperature with a Perkin-Elmer spectrophotometer Model 283B. The spectra were simultaneously digitized and collected in the computer memory of an infrared data station. An automatic difference spectrum was computed by using the DIFFERENCE command to convert both spectra to absorbance units and then to subtract one from the other.

The DIFFERENCE command takes the difference of the spectra in *X* (mixture *M*) and *Y* (component *A* or *C*). The resulting difference spectrum is stored in absorbance in region *Z* (component *C* or *A*). The DIFFERENCE routine also normalizes the data for varying band intensities, a condition that occurs with varying sample thicknesses and concentrations. To enhance the resulting difference spectrum, the ABEX command is used to automatically make the strongest bands.

The spectra of the mixture (Fig. 1) are of the same intensity and exhibit the same sloping base line with the absorption bands clearly resolved at different concentrations. The DIFFERENCE command is used to subtract the spectrum of the known component (*A* or *C*) from the mixture (*M*). After the resulting difference spectrum is expanded, smoothed, and flattened, it is saved on a microfloppy disk. Using the same DIFFERENCE command, Figures 2 and 3 were produced. The sloping base line is present, but in this case, a FLAT routine may be used to flatten the spectra to the highest transmission.

RESULTS AND DISCUSSION

IR spectra of the resins in the region 825–830 cm^{-1} are characteristic absorption bands for the *A* and *C* components but were not the same for those of the mixture, i.e., the IR spectra of the mixture (*M*, *DM*, and *DRM*) were additive. Information about the concentration of a resin to the concentration of other resins in the mixture can be obtained by comparing the wavenumbers and absorbance values of the IR spectra in the region of 827 cm^{-1} . The data presented in Table I can be expressed in terms of percent based on initial sample weight for *A*, *C*, and *M*. The band at 827 cm^{-1} was proved to be independent of the amount of each component in a mixture *M*. Therefore, the relative absorbance in *DM* and *DRM* can be used for the determination of quantitative composition. However, from the extensive study of the degradation of many polymeric materials,¹⁻⁶ a limited range of key degradative processes has now been established. From this range of reactions, it is possible to anticipate the types of processes likely to be important in the deterioration of any polymer system.

All degradative processes originate from an initial bond-breaking reaction. This may represent the total extent of degradation or it may be the prelude to a series of secondary chemical reactions leading to further bond scission, recombination, or substitution reactions. Chemical bonds may be broken by energy input in the form of heat, radiation (light,

Table I Percent Composition of the Anionic and Cationic Resins Mixture by Infrared Spectroscopy

Experimental Series	Kind of Resin	Absorbance	Concentration (%)	
			A	C
1	A	0.442 (825 cm ⁻¹)	100.0	—
2	C	0.317 (830 cm ⁻¹)	—	100.0
3	M	0.745 (827 cm ⁻¹)	50.2	49.9
4	DM	0.715 (827 cm ⁻¹)	38.6	45.3
5	DRM	0.658 (827 cm ⁻¹)	27.5	42.1

A, anionic resin IRN-78 not used. C, cationic resin IRN-77 not used. M, mixture not used of A and C in proportion 1 : 1. DM, mixture used of A and C decontaminated. DRM, mixture used of A and C decontaminated and regenerated the vibrational frequency is shown in parentheses.

γ , X-rays; electron beam), mechanical action, etc. Of these, ionizing radiation can profoundly alter the molecular structure and macroscopic properties of polymeric materials. In almost all cases, the absorbed radiation dose triggers a complex set of events.⁷ For wavelengths below 290 nm, the aromatic ring absorbs directly, leading to surface yellowing and cross-linking.⁸ For wavelengths above 295 nm, i.e., solar irradiation, photoreactions result from impurities introduced during processing or storage.⁸ At wavelengths above 295 nm, direct photocleavage of tertiary C—H occurs. On the other hand, when polymeric materials are irradiated in the presence of oxygen, the rate of degradation and the nature of degradation can be strongly influenced by the dose rate. Lower dose rates often increase oxidation and chain-scission yields and result in more extensive material degradation per equivalent absorbed dose.⁹⁻¹² In addition, degradation of irradiated materials of-

ten continues, in storage or in use, long after the material has been removed from the radiation environment. This effect is due to continuing free-radical-mediated oxidation. Significant postirradiation oxidation effects may take place over weeks or years and may result in degradation that is much more extensive than that which was the immediate effect of the radiation. This fact supports the contention that the ion-exchange groups and all the resins are progressively dissociated due to the chemical environment and that permanent change occurs in the ion-exchange material after the resins have been used, decontaminated, and regenerated.

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