Note

A paramagnetic resonance method for detection of copper in cellulose*

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(Received June 7th, 1971)

Shields, Ard, and Gordy[1] reported the microwave detection of manganese and copper in plant materials. Ingram and Bennett[2] decided that the paramagnetic resonance was associated with the presence of chlorophyll and hemoglobin, and related their results to the detection of copper, iron, manganese, cobalt, and nickel. We have described the electron-spin resonance spectrum of sodium hydroxide–cellulose systems, and suggested that, on addition of sodium hydroxide to cellulose, the natural cellulose–copper chelate is dissociated, and that the trace quantity of copper iberated generates the spectrum[3]

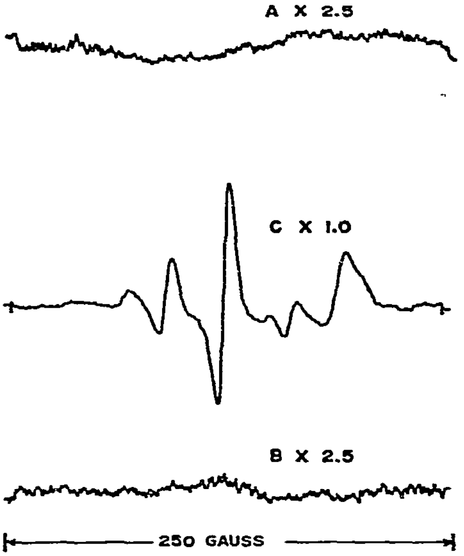

Fig. 1. E.p.r. spectra generated by (A) 5M sodium hydroxide, (B) cotton cellulose, and (C) sodium hydroxide (5M)–cotton cellulose at −100°. (The magnetic field increases from left to right.)

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*Presented at the Symposium on Chemical Analysis of Fiber Systems, 159th National Meeting of the American Chemical Society, New York, New York, September 7–12, 1969.

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We have extended these investigations to develop a paramagnetic resonance (e.p.r.) method for the estimation of copper in cellulose, both with and without ashing before the estimation is made. The e.p.r. method is a dynamic method in which the energy associated with the spin and moment of an unpaired electron is measured. Each paramagnetic element generates a specific resonance spectrum that is different from those generated by free radicals. Consequently, by using the e.p.r. method, trace quantities of a paramagnetic element can be detected in the presence of species that have unpaired electrons[4].

The paramagnetic resonance spectrum (of copper) generated when cotton cellulose is treated with sodium hydroxide (5M), the system is frozen in liquid nitrogen, and the temperature is raised to −100° was recorded at −100°, and is shown in Fig. 1C. Separately, neither the sodium hydroxide solution (Fig. 1A) nor the cotton cellulose (Fig. 1B) generated a paramagnetic resonance spectrum. As reported previously, the spectrum, shown in Fig. 1C, is almost identical with that generated when Cu^{2+} ions are present in sodium hydroxide solution. The concentration of copper present in cellulose was proportional to the peak-to-peak value of the principal line of the spectrum (see Fig. 1C). Increased precision was obtained if a weighed quantity of cellulose was ashed[5], the ash dissolved in dilute hydrochloric acid, the suspension filtered through sintered glass, and the filtrate made to volume by the addition of distilled water and sodium hydroxide solution. In this way, the quantity of copper in

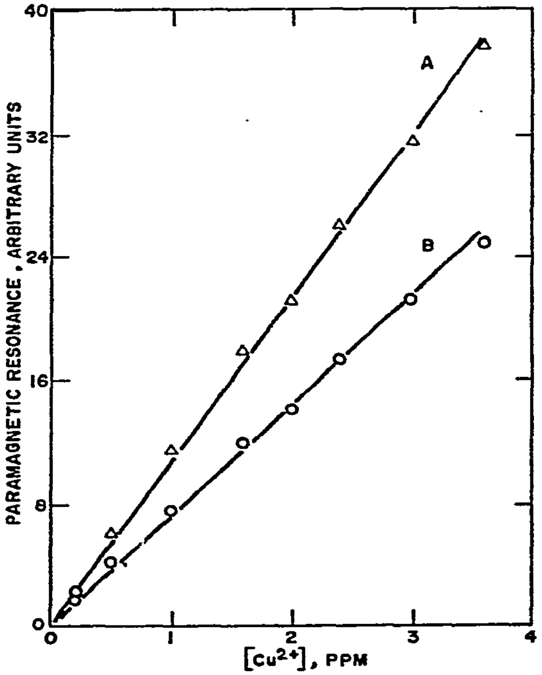

Fig. 2. E.p.r. (peak-to-peak value of principal line) *versus* concentration of cupric ion in 5M sodium hydroxide at −100°. [Modulation amplitudes are (A) 800 and (B) 1600.]

a given amount of cellulose could be more precisely placed in the sensitive part of the microwave cavity than when a cellulose sample in the solid state was placed in the cavity.

A standard reference curve for paramagnetic resonance *versus* concentration of Cu^{2+} in sodium hydroxide solution was prepared (see Fig. 2). By considering the instrumental adjustments and experimental dilutions, the peak-to-peak value of the principal line of the spectrum for the unknown sample was measured, and the concentration of copper was determined from the reference curve.

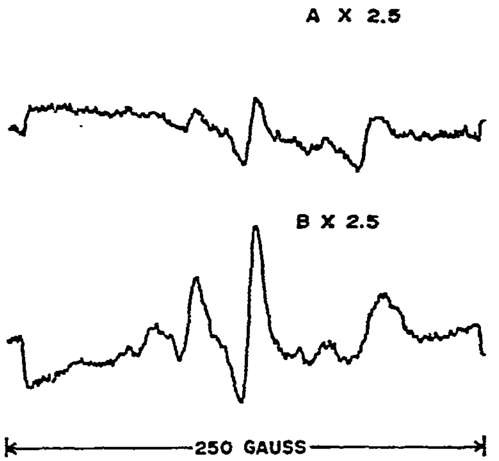

Fig. 3. E.p.r. spectra generated by (A) sodium hydroxide (5M)-purified cotton cellulose, and (B) sodium hydroxide (5M)-regenerated cellulosic fibers at −100°. (The magnetic field increases from eft to right.)

Typical e.p.r. spectra for purified cotton cellulose (Fig. 3A) and regenerated cellulosic fibers (Fig. 3B), both treated with sodium hydroxide solution, are shown in Fig. 3. Typical values for the copper present in purified cotton cellulose are: 2.6 p.p.m. (e.p.r. method), 2.0 p.p.m. (neutron activation analysis)[6], and 8.6 p.p.m. (atomic absorption analysis)[7].

EXPERIMENTAL

Deltapine cotton in the form of 7 s/3 yarn (grey) was used as received; also, part of it was purified[8] to yield cellulose (mol. wt. 700,000)[9]. Regenerated cellulosic fibers were obtained from a commercial source. Copper-free distilled water was used in the preparation of solutions of copper sulfate and sodium hydroxide from reagent-grade chemicals.

The e.p.r. spectra were recorded with a Varian 4502-15 EPR spectrometer system*. The system was equipped with cell accessories for aqueous solutions and

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*Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers.

solid samples, and a variable temperature device. Spectra at −100° were recorded in the form of the first derivative of the absorption line. At this temperature and this frequency of the spectrometer, absorption of microwave power by the aqueous system was minimized or eliminated, because of lowering of the dielectric constant of the system to near zero.

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