The presence of formaldehyde (FA) in some endodontic sealers and its release after manipulation have been studied. Inasmuch as one aim of endodontic treatment is the repair of inflamed periapical tissues, even small quantities of FA may act as an irritant, impeding or retarding regeneration. It has been shown that some endodontic sealers, such as Endomethasone and N2, which contain FA, may cause tissue necrosis and inflammation, thereby slowing tissue repair. Ingredients that do not contain FA in their formulas may form and release the FA molecule during the chemical reaction of setting. For example, after the mixing of AH 26, FA is released.

New resin-based sealers that presumably do not contain FA have become commercially available. According to manufacturers, AH Plus and Top Seal do not release FA, although this has not been demonstrated experimentally.

The objective of this study was to evaluate AH 26, Endomethasone, AH Plus, and Top Seal sealers for the presence of FA after mixing.

MATERIAL AND METHODS
AH 26 (De Trey Frères SA, Zurich, Switzerland), Endomethasone (Sociétées-Septodont, Paris, France), AH Plus (Dentsply DeTrey GmbH, Konstaz, Germany), and Top Seal (formula identical to AH Plus; Dentsply/Maillefer, Ballaigues, Switzerland) were analyzed. FA (Merck SA Ind Quim, Rio de Janeiro, Brazil) and paraformaldehyde (Merck SA Ind Quim) were used as standards (positive controls) against which the sealers were compared.

The sealers were mixed according to the manufacturers’ instructions and remained at room temperature for 72 hours to allow for completion of the setting reaction. Five samples of each sealer were prepared. To imitate normal clinical conditions, humidity was not controlled.

Electronic spectra
The ultraviolet (UV) and visible spectra of the sealers were obtained through use of a spectrophotometer (Hitachi model U-3501). A mass of 0.05 g of each sealer was placed in 50 mL of deionized water, agitated for 30 minutes, and subsequently filtered by means of quantitative filter paper to eliminate solid particles. All spectra were obtained at room temperature through use of a 1-cm quartz cell.
Infrared spectroscopy

Under suitable conditions, FA forms a polymer called paraformaldehyde, which maintains the basic structure of its precursor. For comparison, paraformaldehyde could be analyzed spectroscopically, but its low solubility in water makes it impossible to observe characteristic bands in the UV-visible range. Thus, it was necessary to analyze paraformaldehyde presence and levels through use of infrared spectroscopy. Almost any compound having covalent bonds will absorb various frequencies of electromagnetic radiation in the infrared region of the spectrum. Every different type of bond has a different natural frequency of vibration, because the same type of bond in 2 different compounds is in a slightly different environment. No 2 molecules of different structures will have exactly the same infrared absorption pattern or infrared spectrum.

The infrared spectra of the sealers were obtained by means of a Nicolet recording spectrophotometer (model Protege 460). Infrared spectra of solid samples were obtained with potassium bromide pellets. The sample of each sealer was finely ground, and approximately 0.05 g of the powder was compressed to form a homogeneous pellet; this pellet was then analyzed. A blank bromide pellet of identical thickness was used as a reference to minimize any absorption. Polystyrene standards were used to calibrate spectra.

The presence of FA was analyzed by both UV-visible and infrared spectroscopy. In an aqueous solution, the existence of bands in the UV range ($\lambda = 288; 242$ nm; Fig
1) was used to indicate the presence of FA. In the solid state, the bands at 2983, 2923, and 1383 cm⁻¹ were used in the characterization of samples containing FA or its derivative, paraformaldehyde. Each sample was analyzed and graphs were obtained. Only 1 graph is reproduced for each sealer because all samples proved to be similar.

RESULTS

The concentration of aldehyde was greatest in sealer AH-26; however, because of the other absorptions existent in the spectrum of this material, it is not possible to report the exact quantity of FA in the samples. The technique used for analysis of the material in the solid state, the bands at 2983, 2923, and 1383 cm⁻¹ were used in the characterization of samples containing FA or its derivative, paraformaldehyde. Each sample was analyzed and graphs were obtained. Only 1 graph is reproduced for each sealer because all samples proved to be similar.
state allowed only qualitative characterization, indicating the presence or absence of FA or its derivative.

The electronic spectrum of the positive control standard (FA in water) is represented in Fig 1. Two bands were observed in the ultraviolet range, one at 288 nm, characterized as n–π*, and the other, of a higher intensity, at 242 nm, characterized as π–π*. Spectra of the sealers AH 26 and AH Plus in water (experimental specimens) are shown in Figs 2 and 3. The spectrum of Top Seal was similar to that of AH Plus.

The infrared spectroscopic analyses of paraformaldehyde, AH Plus, AH 26, and Endomethasone with KBr pellets are shown in Figs 4 through 7. Analysis was used to compare the infrared spectrum of the sealers with that of paraformaldehyde. The bands assigned at 2983 and 2923 cm⁻¹, characterized as C-H stretching, as well as at 1383 cm⁻¹, characterized as CH₂ deformation, were also found in the spectra of Endomethasone and AH 26; however, the bands were not found in the infrared spectrum of AH Plus (Figs 4 through 7) and Top Seal (data not shown).

The spectroscopic data show that the infrared spectrum of AH 26 had an intense band at 1240 cm⁻¹. Other bands of lower intensity at 1470 and 1380 cm⁻¹ were similar to those observed in the spectrum of paraformaldehyde. Thus, both the UV-visible and infrared spectroscopy data were consistent with the presence of FA in AH 26 sealer.

**DISCUSSION**

Currently, the technique of choice for obturation involves gutta-percha in combination with a sealer, inasmuch as gutta-percha alone does not ensure a hermetic seal. Root canal sealers are important for the hermetic sealing of the canal and consequently for success, acting as agents between the gutta-percha and the root canal wall. They fill in the spaces not reached by the gutta-percha because of its physical limitations.

An important requirement for a sealer is biologic compatibility; the sealer is often in direct contact with apical and periapical tissues and should not induce an inflammatory or immune response. Mutagenic properties have been discussed for sealers that contain FA and paraformaldehyde. Zinc oxide and eugenol-based sealers, modified with paraformaldehyde, become antigenically active. The American Consumer Products Commission and the National Academy of Sciences warn of the risks of products releasing FA.

The release of FA by AH 26 sealer has been demonstrated by Spångberg et al. The formation of FA from this sealer is attributed to the chemical reaction that occurs between bisphenol A resin and hexamethylene-tetramine. Spångberg et al observed that the release was greatest during the first 48 hours.

Even though we prepared the cements under conditions similar to those of the clinic, it is important to note that experimental conditions of temperature and
humidity influence the chemical reaction of FA. With high humidity and temperature, as in vivo, increased FA formation is expected, because these factors are important in the development of any reaction.

As expected, the electronic spectrum of AH 26 is closely analogous to that of FA, with the ultraviolet region dominated by a $\pi - \pi^*$ internal ligand transition. Identification of FA in the sealers was obvious due to the presence of a band in the 290-nm region; this also was observed in the electronic spectrum of FA (Fig 1). However, it was not possible to find any evidence of FA by means of electronic spectrum analysis of Top Seal, Endomethasone, or AH Plus (Fig 3). Because paraformaldehyde is a component of Endomethasone, the UV-visible spectrum should be extended for a technique that permits analysis in the solid state. Because the polymerization reaction of FA leads to the insoluble product paraformaldehyde, the spectral analysis was also extended to infrared spectroscopy.

Similar results were obtained with infrared spectroscopy. Because FA is extremely volatile, it is probable that it is associated with the components of the sealer, such as resin. This observation suggests that the most plausible comparison would be with paraformaldehyde.

Although the UV-visible spectrum of AH-Plus did not correspond to the presence of FA (contrary to the findings with AH-26 and Endomethasone), it is possible to attribute a small quantity of FA released by AH-Plus with infrared spectroscopic analysis (Fig 5). Because the UV-visible spectroscopy technique presented sensitivity to a minimum concentration of $10^{-5}$ mol/L, it is possible that the concentration of FA in AH-Plus is less than $10^{-5}$ mol/L and may be considered negligible in relation to the quantity observed with AH-26 and Endomethasone.

New plastic, resin-based sealers have recently been developed; among these are AH Plus and Top Seal, which according to their manufacturers maintain the same physical-chemical properties that characterize AH 26. However, our analysis of samples of AH Plus and Top Seal sealers with UV-visible and infrared spectroscopy showed a minimum concentration of an aldehyde derivative.

REFERENCES

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