

# Infrared study of the interaction of dental polycarboxylate cements with tooth structure and some metals

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The interaction of three commercial zinc polycarboxylate cements with tooth structure was investigated by using infrared spectroscopic techniques. The obtained data revealed that the cements interact with enamel and ionic bonds are formed between calcium ions in enamel and carboxyl groups in polycarboxylic acid. The interaction depends on the percentages of ZnO content in the powders and of carboxylic acid in the liquids of these cements. The results provided some evidence that the cements also may interact with dentin but to a lesser extent than with enamel. The interaction of the cements with the metals copper and nickel or with  $\text{Cr}_2\text{O}_3$ , was also studied.

## 1. Introduction

The composition and properties of zinc polycarboxylate cements which were developed for cementing full-crown restoration and for bridge work on teeth with vital pulps, have been investigated by a number of workers [1-4]. Wilson and Mesley [5] concluded that zinc polycarboxylate cement is a simple salt and the  $\text{COO-Zn}$  bond is purely ionic with no covalent or chelated character.

The fact that these cements can adhere to enamel and dentin was demonstrated by several investigators [6-8]. Wilson *et al.* [9] stated that the adhesion of polyelectrolyte cements to enamel is achieved by the displacement of the phosphate ions in the enamel surface, by carboxylate groups pendent on the polymer.

Various opinions have been expressed with regard to the nature and extent of the bonding of the cements to dental casting alloys [10-12]. The chemical adhesion of the cement to casting alloys would greatly improve the ability of the cement to seal against penetration of oral fluids. Saito *et al.* [12] stated that polycarboxylate cement seems to form a stronger bond with chemically active substitute alloys such as copper, nickel-chromium and silver-tin-zinc alloys than with chemically stable precious alloys. Gold alloys, which have other elements such as copper, can adhere to the polycarboxylate cement. It is possible that the copper may provide a reactive site with which the cement can interact.

However, the exact mechanism of the adhesion to the tooth structure and to dental casting alloys is not entirely known and remains a subject for speculation. Therefore, the present study is undertaken to obtain further information about the interaction of zinc polycarboxylate cements with tooth structure and with

$\text{Cr}_2\text{O}_3$ , nickel or copper. The study will be carried out by using quantitative infrared spectroscopic techniques.

## 2. Materials and methods

The three commercial zinc polycarboxylate cements, PCA, Durelon and Carboxylon were used in the present study. The percentages of zinc oxide and magnesium oxide in the powder and of polyacrylic acid in the liquids are given in Table I.

The powders also contain traces of other elements but with concentrations less than 100 part per million. Spec-pure zinc oxide was also mixed with each liquid of the three cements with the same ratio of cements 1, 2 and 3 to form cements 4, 5 and 6.

10 mg powder of each of enamel, dentin, copper, nickel and  $\text{Cr}_2\text{O}_3$  were mixed with 80 mg commercial zinc oxide powder. This mixture was then added to 90 mg of each of the liquids.

The infrared spectra were recorded on Beckman Spectrophotometer 4250 by using the KBr disc techniques.

## 3. Results and discussion

The infrared spectra of the three zinc polycarboxylate cements are shown in Fig. 1. It appears from this figure that the spectra of the three cements exhibit absorption bands at the frequencies  $1410, 1560\text{ cm}^{-1}$  due to the symmetric and asymmetric stretching vibrations of the  $\text{COO}^-$  structure, respectively. The spectrum of cement 1 also showed a strong shoulder at about  $1700\text{ cm}^{-1}$ , whilst that of cement 2 shows a weak one at the same frequency. The appearance of this shoulder, which is associated with the acid C-O stretching vibration, indicates that both cements 1 and 2 contain a small amount of residual acid. Fig. 1

TABLE I

Symbols	Cement	% ZnO	% MgO	% Polyacrylic acid	% Water	Powder:liquid (mg)
Cement 1	PCA	86	2.65	31	68	1:1.125
Cement 2	Durelon	93.6	0.1	39	59	1:1.125
Cement 3	Polycarboxylon	98.1	0.21	42	58	1:1.125

indicates also that the spectra of all cements show an absorption band of medium intensity at the frequency  $450\text{ cm}^{-1}$ , which can be ascribed to Zn-O vibration. The presence of this band can be attributed to the presence of excess zinc oxide dispersed in the zinc polycarboxylate cements.

To prove this fact the amount of powder in the mixture of polycarboxylate cement was reduced to one third and another cement was formed. The spectrum of this cement is shown in Fig. 1, spectrum 4. It is clear from Fig. 1 that there is no evidence of the Zn-O band in spectrum 4.

The foregoing data lead to the conclusion that the COO-Zn bond is purely ionic, with no covalent or chelate character. This result is in good agreement with the results reported in the literature [5].

The zinc polycarboxylate cements were then combined to the enamel powder. Fig. 2 presents the infrared spectra of these samples. It is apparent from this figure that these samples absorb at the frequencies  $950$  and  $1030\text{ cm}^{-1}$  which are the diagnostic frequencies of apatite.

The resultant combined spectra do not show that the absorption frequencies of zinc polycarboxylate cements have changed in the process. It is not possible to show directly that a wavelength shift or intensity change of the stretching C-O bands occurs, since such changes can occur as a result of two unresolved components. However, the changes are likely to be accompanied by change in absorption intensity and hence the absorbances of the zinc polycarboxylate cements and of enamel-zinc polycarboxylate samples were measured at  $1560\text{ cm}^{-1}$ . In order to establish this on a quantitative basis and since the CH group is unaffected by the modification, the ratio of the absorbance of the absorption band at  $1560\text{ cm}^{-1}$  to that of the C-H stretching band at  $2950\text{ cm}^{-1}$  was determined. The absorbances were measured by using the base line method. A base line was drawn across the  $1560\text{ cm}^{-1}$  band from  $1475\text{ cm}^{-1}$  to  $1775\text{ cm}^{-1}$ . The base line for the  $2950\text{ cm}^{-1}$  was taken as the horizontal line which passes through the lower frequency side of this band at  $2400\text{ cm}^{-1}$ . The determined values of absorbances and ratios are given in Table II. This table reveals that

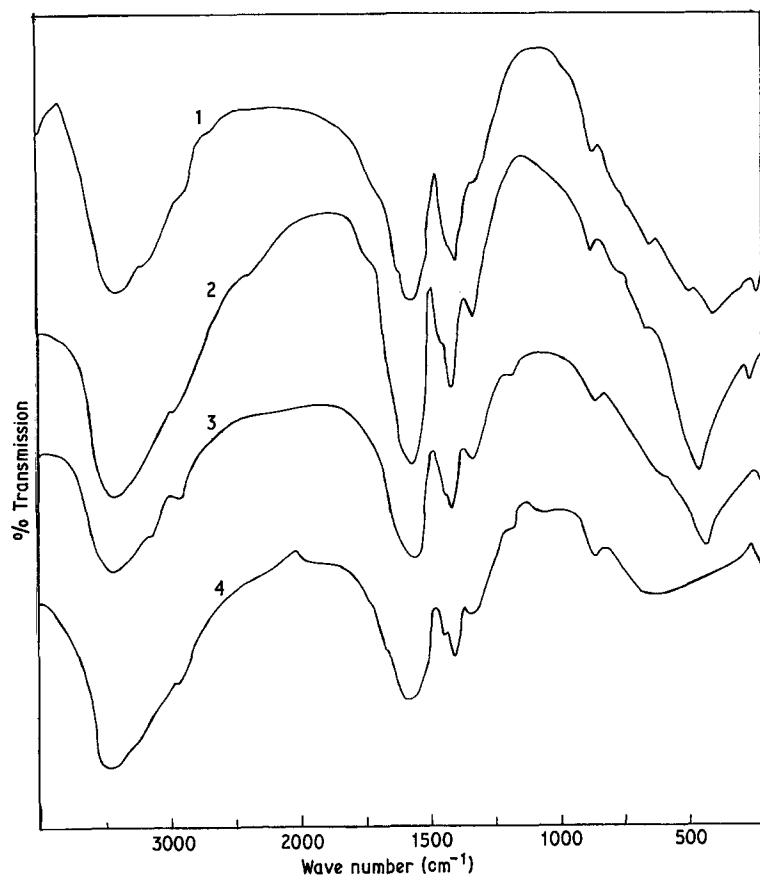


Figure 1 Infrared spectra of: 1, cement 1; 2, cement 2; 3, cement 3; 4, cement 1 with excess liquid.

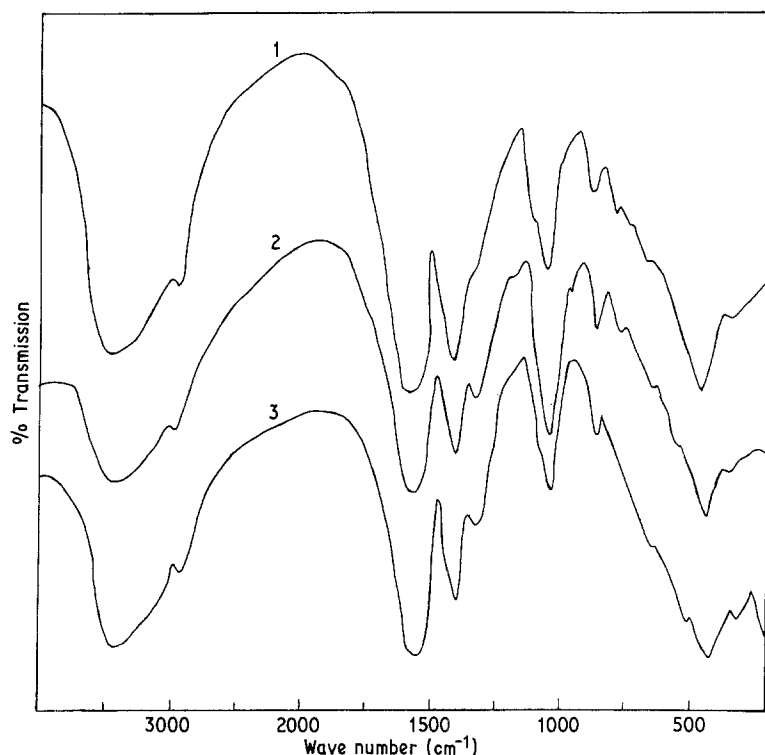


Figure 2 Infrared spectra of mixtures of cements 1, 2 and 3 with enamel: 1, cement 1; 2, cement 2; 3, cement 3.

the values of the ratio  $a_{1560\text{ cm}^{-1}}/a_{2950\text{ cm}^{-1}}$  for cements 1, 2 and 3 are 1.40, 1.56 and 1.65, respectively. It is clear that these values are directly proportional to the percentage of polycarboxylic acid in liquids and also to the zinc oxide content in powders. The values of this ratio for enamel-zinc polycarboxylate samples are about 1.56, 1.70 and 1.61. The increments in these values of the cases of samples 1 and 2 suggest that new absorption bands have arisen in the spectra of these two samples near  $1560\text{ cm}^{-1}$ . This absorption may be due to ionized carboxyl groups produced by interaction of polycarboxylic acid with enamel. This result provides strong evidence for the formation of ionic bonds between the calcium ions in enamel and the polycarboxylic acid. It seems very important to mention that this interaction took place only in cases of cements 1 and 2 which contain a small amount of free carboxylic acid as indicated by their infrared spectra (Fig. 1).

The other three cements (4, 5 and 6) were formed by mixing spec-pure zinc oxides (instead of the commercial powders) with the three liquids in the same ratios of powder to liquid. It can be seen from Fig. 3 that the spectrum of cement 2 exhibits a hint of shoulder at about  $1700\text{ cm}^{-1}$ , while the spectrum of cement 3 shows a strong shoulder at the same frequency. This means that both cements contain small amounts of residual acid. The Zn-O band appears at  $450\text{ cm}^{-1}$  in the spectra of the three cements.

The ratio  $a_{1560\text{ cm}^{-1}}/a_{2950\text{ cm}^{-1}}$  was determined for each cement and is given in Table II. The values of this ratio for cements 4, 5 and 6 are 1.02, 1.23 and 1.48, respectively.

It is evident that the value of  $a_{1560\text{ cm}^{-1}}/a_{2950\text{ cm}^{-1}}$  increases as the percentage of carboxylic acid increases. It appears also that the ratio in the case of pure powders assumes a lower value than that for commercial powders. This result provides considerable

TABLE II The absorbances of the  $1560\text{ cm}^{-1}$  and  $2950\text{ cm}^{-1}$  bands and their ratios

Sample	Absorbance of $1560\text{ cm}^{-1}$ band	Absorbance of $2950\text{ cm}^{-1}$ band	$a_{1560\text{ cm}^{-1}}/a_{2950\text{ cm}^{-1}}$
Cement 1	0.090	0.064	1.40
Cement 1: enamel	0.081	0.049	1.65
Cement 1: dentin	0.105	0.078	1.34
Cement 2	0.151	0.097	1.56
Cement 2: enamel	0.079	0.046	1.70
Cement 2: dentin	0.166	0.0148	1.12
Cement 3	0.093	0.056	1.66
Cement 3: enamel	0.139	0.087	1.61
Cement 3: dentin	0.181	0.122	1.48
Cement 4	0.106	0.102	1.07
Cement 4: enamel	0.143	0.149	0.99
Cement 5	0.110	0.089	1.23
Cement 5: enamel	0.119	0.092	1.30
Cement 6	0.092	0.62	1.48
Cement 6: enamel	0.143	0.086	1.66

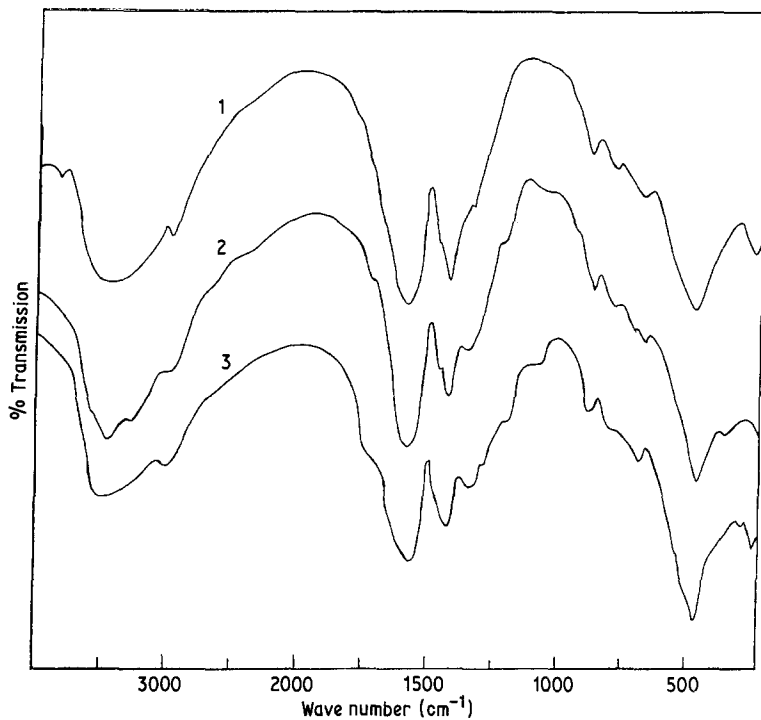


Figure 3 Infrared spectra of: 1, cement 4; 2, cement 5; 3, cement 6.

evidence for the formation of ionic bonds between magnesium ions or other metal ions in the commercial powders and the polycarboxylic acid in polycarboxylate cement.

The pure zinc oxide polycarboxylate cements were then mixed with enamel powders. The infrared spectra of these samples are shown in Fig. 4. The values of the ratio  $a_{1560\text{cm}^{-1}}/a_{2950\text{cm}^{-1}}$  for these samples are 0.99, 1.30 and 1.64 for cements 4, 5 and 6, respectively. These values show that the ratio for cement 4 did not change upon mixing with enamel, but the values of this ratio for cements 5 and 6 increased. This means that cements 5 and 6 interact with enamel. This may be due to the presence of a small amount of residual acid in both cements. To confirm this result, a difference spectrum was recorded. A KBr disc containing the cement was placed in the reference beam and a disc

containing the enamel-cement sample was placed in the sample beam. The difference spectra are shown in Fig. 5. This figure indicates that the difference spectrum of cement 5 shows two weak bands at 1560 and 1410  $\text{cm}^{-1}$ , whereas the spectrum of cement 6 exhibits two strong bands at the same frequencies. On the other hand, there is no evidence for any absorption at these frequencies in the case of cement 4. The Zn-O band is absent from these spectra.

Based on the foregoing data it could be concluded that in the case of pure zinc oxides, ionic bonds are formed between calcium ions in enamel and carboxyl groups of polycarboxylic acid in cements 5 and 6.

The three cements 1, 2 and 3 were then mixed with dentin. Fig. 6 presents the infrared spectra of the mixtures. It can be easily seen from Fig. 6 that the spectrum of the mixture of cement 1 with dentin

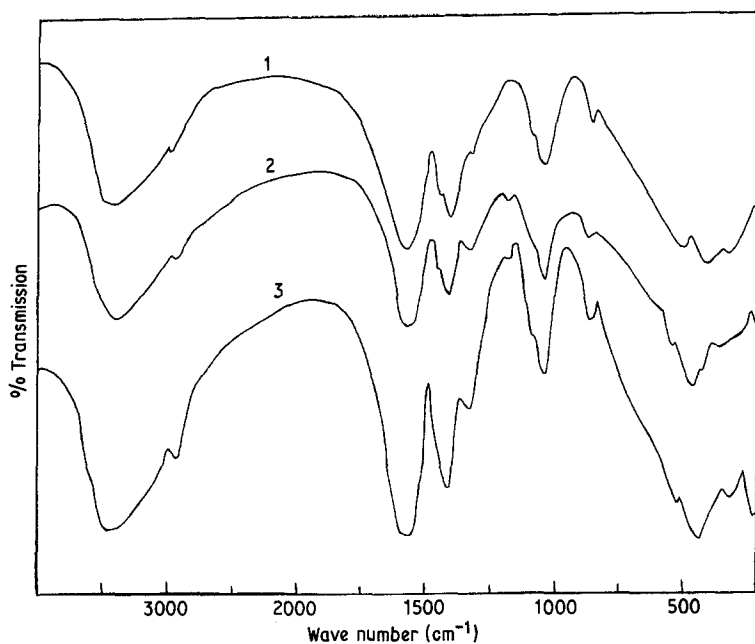


Figure 4 Infrared spectra of mixture of cements 4, 5 and 6 with enamel: 1, cement 4; 2, cement 5; 3, cement 6.

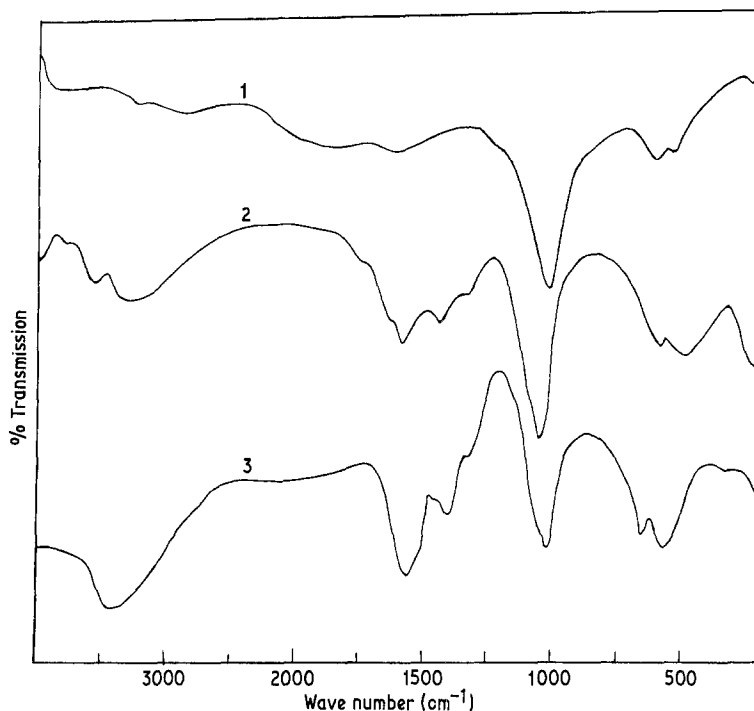


Figure 5 The difference spectra of: 1, cement 1 with enamel and cement 1; 2, cement 2 with enamel and cement 2; 3, cement 3 with enamel and cement 3.

exhibits strong absorption at about  $1700\text{ cm}^{-1}$  which is associated with the free carboxylic acid. The spectrum of the mixture of cement 2 and dentin shows only a weak shoulder at the same frequency. The  $1700\text{ cm}^{-1}$  band has no evidence in the spectrum of the mixture of cement 3 and dentin. The spectra of these mixtures show the P-O stretching band of apatite at  $1030\text{ cm}^{-1}$ .

The infrared spectrum of dentin was also recorded. It was observed that this spectrum shows, in addition to the characteristic bands of apatite, two weak bands at  $1650$  and  $2950\text{ cm}^{-1}$  and a very weak one at  $1550\text{ cm}^{-1}$ . The presence of these bands confirms the presence of organic content in the dentin. Thus, it should be expected that this organic content will play a role in the interaction of these cements with dentin.

The values of the ratio  $a_{1560\text{ cm}^{-1}}/a_{2950\text{ cm}^{-1}}$  are 1.34, 1.12 and 1.48 for cements 1, 2 and 3, respectively (Table I). It seems very important to mention here that mixing of the cements with dentin reduces the value of this ratio. This result can be interpreted on the basis of the mechanism of adhesion between the cements and dentin, suggested by Wilson [8]. Collagen (dentin) contains some branch chains that terminate in carboxylic acid groups, and others that terminate in amino groups. The former can link to the cement mass by metal ion bridging, while the latter groups bond by hydrogen bridges. This result would explain the poorer adhesion to dentin which has a much higher organic content than enamel. However, the above results are in good correlation with the results reported

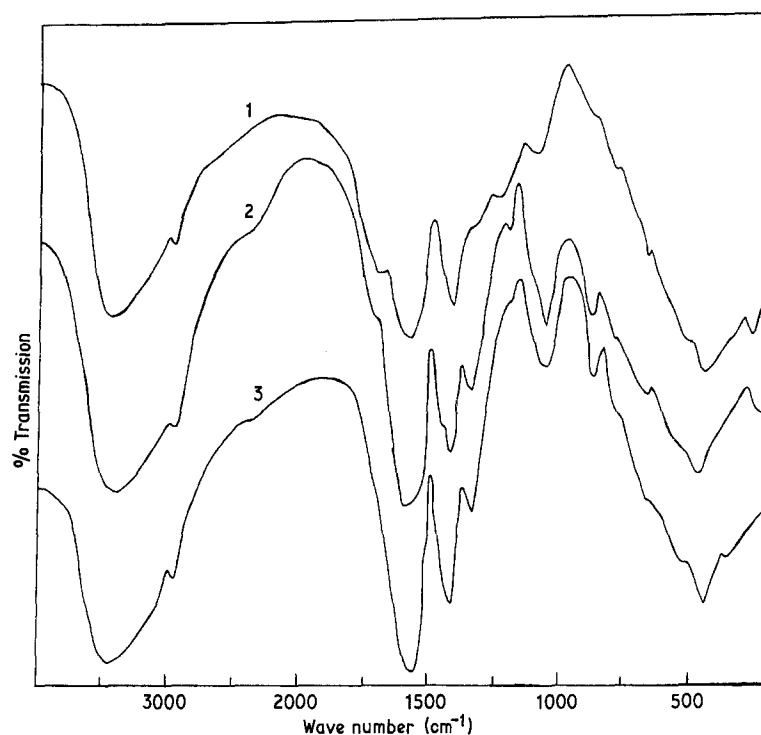


Figure 6 Infrared spectra of mixtures of cements 1, 2 and 3 with dentin: 1, cement 1; 2, cement 2; 3, cement 3.

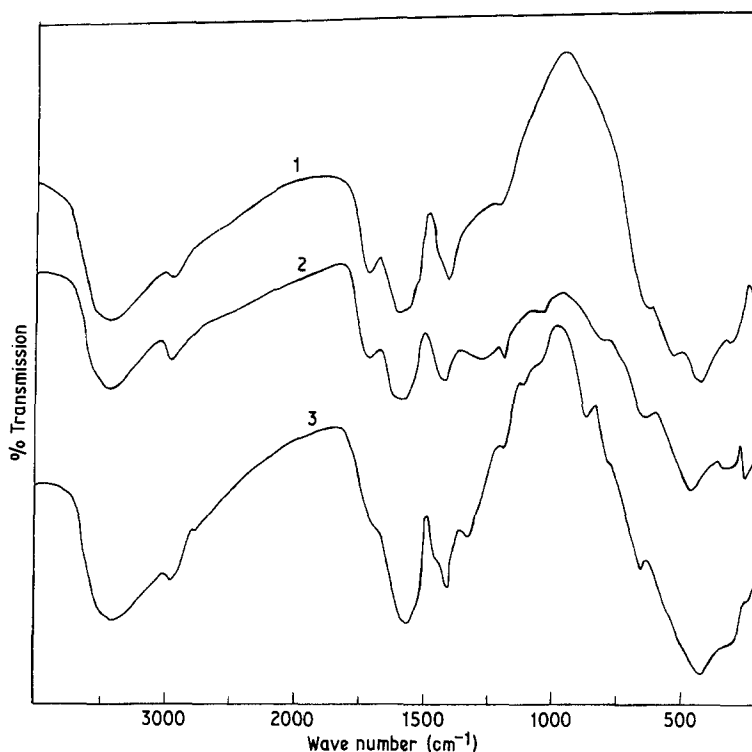


Figure 7 Infrared spectra of mixture of cements 1, 2 and 3 with  $\text{Cr}_2\text{O}_3$ : 1, cement 1; 2, cement 2; 3, cement 3.

by several workers who have shown that polycarboxylate cement exhibits long-term adhesion to tooth enamel in the presence of water and to a lesser extent to dentin.

In the present study the chemical reaction between the three cements under investigation and the metals copper and nickel, and  $\text{Cr}_2\text{O}_3$ , has been taken into consideration. These metals were added to the cements in the ratio, cement : metal, 1:17. The infrared spectra of the mixtures were recorded. The infrared spectra of the mixture of  $\text{Cr}_2\text{O}_3$  and cements are given in Fig. 7 as an example. It is clear from this figure that, these spectra exhibit a definite absorption band at  $1700\text{ cm}^{-1}$  which is associated with the C–O stretching vibration of COOH groups. The spectra of cement 3 show only a definite shoulder at the same frequency. It was noticed that the intensity of this band decreased in the order: intensity for sample containing copper > intensity for sample containing  $\text{Cr}_2\text{O}_3$  > intensity for the sample containing nickel. However, the absorbances of the bands at  $1560$  and  $1700\text{ cm}^{-1}$  were determined using the base-line method. Base lines were drawn from  $1475$  to  $1775\text{ cm}^{-1}$  and from  $1650$  to  $1775\text{ cm}^{-1}$  across the respective bands. The ratio of the absorbance of the  $1700\text{ cm}^{-1}$  band to that of the  $1560\text{ cm}^{-1}$  band was determined for each sample. The determined values are given in Table III. This table indicates that for any given metal the amount of residual acid in the three cements decreases in the order  $\text{Cu} > \text{Cr}_2\text{O}_3 > \text{Ni}$ .

In order to throw more light on the mechanism of reaction, each of these metals was mixed with each of the liquids with the ratios given below:

1. 80 mg metal with 90 mg liquid;
2. 40 mg metal and 40 mg ZnO with 90 mg liquid;
3. 20 mg metal + 60 mg ZnO with 90 mg liquid.

The IR spectra of the mixtures are shown in Fig. 8 (spectra for  $\text{Cr}_2\text{O}_3$  as an example). It can be readily

seen from Fig. 8 that addition of  $\text{Cr}_2\text{O}_3$  to the liquid causes no shift to the maximum of the  $1700\text{ cm}^{-1}$  peak. The Cr–O band occurs at  $625\text{ cm}^{-1}$ . Addition of 50% ZnO and 50%  $\text{Cr}_2\text{O}_3$  results in the appearance of the  $\text{COO}^-$  band at  $1560\text{ cm}^{-1}$  and the band at  $1700\text{ cm}^{-1}$ ; the former band being more intense than the latter. The Cr–O band is still present at  $625\text{ cm}^{-1}$ ; the Zr–O band is still absent. Addition of only 25%  $\text{Cr}_2\text{O}_3$  and 75% ZnO results in the appearance of a strong  $\text{COO}^-$  band with a strong shoulder due to the COOH groups at  $1700\text{ cm}^{-1}$ , in addition to the Cr–O band. The absorption due to Zn–O is not clear. A similar mechanism for copper and nickel has also been observed.

These data mean that the addition of  $\text{Cr}_2\text{O}_3$ , nickel or copper to zinc oxide powder results in the reappearance of the  $1700\text{ cm}^{-1}$  band corresponding to the unionized acid groups. The ratio of the absorbances at  $1700\text{ cm}^{-1}$  to that at  $1560\text{ cm}^{-1}$  provides strong evidence that the amount of the free acid group depends on the chemical activity of the added elements. Based on these data one can suggest that the adhesion of polycarboxylate cements to dental casting alloys, which has been accepted by several workers, would be attributed to the residual free acid groups in the cement.

However, at the present time the exact mechanism of interaction is not completely clear and in order to find out any kind of general rule further experimental investigation is necessary.

TABLE III

	$a_{1700\text{ cm}^{-1}}/a_{1560\text{ cm}^{-1}}$		
	Cement 1	Cement 2	Cement 3
Cu	0.36	0.34	0.23
$\text{Cr}_2\text{O}_3$	0.33	0.32	0.13
Ni	0.21	0.20	0.04

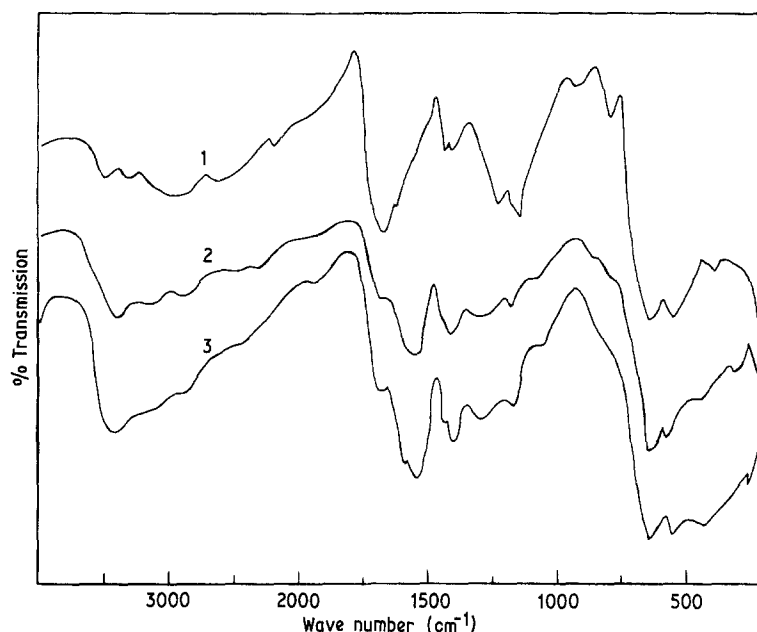


Figure 8 Infrared spectra of mixtures of ZnO, Cr<sub>2</sub>O<sub>3</sub> and liquid polycarboxylic acid. 1, 80 mg Cr<sub>2</sub>O<sub>3</sub> + 90 mg liquid, 2, 40 mg ZnO + 40 mg Cr<sub>2</sub>O<sub>3</sub> + 90 mg liquid; 3, 60 mg ZnO + 20 mg Cr<sub>2</sub>O<sub>3</sub> + 90 mg liquid.

#### 4. Conclusion

Based on the experimentally obtained data one can conclude that the COO<sup>-</sup>-Zn bond in polycarboxylate cements is purely ionic with no covalent or chelate character. The polycarboxylate cements interact with tooth enamel and ionic bonds are formed between the calcium ions in enamel and carboxylate groups in carboxylic acid. The interaction depends on the percentage of ZnO content in the powder and of the polycarboxylate acid in the liquid. The results showed some evidence that the cements may also bond to the collagen of the dentin. But the interaction of the cements with dentin is weaker than with enamel. The bonding to collagen may involve both hydrogen and ionic bonding. Addition of Cr<sub>2</sub>O<sub>3</sub>, nickel or copper to the cement powder results in the formation of residual free acid groups in the cements. The amount of these unionized acid groups depends on the chemical activity of the added elements. At the present time it would be premature, on the basis of the experimentally obtained data, to draw definite conclusions about the exact mechanism of reaction between these metals and the cements under investigation.

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