

# Notes

## Thermal & Infrared Analyses of Calcium & Lead Hydroxylapatites & Their Solid Solutions

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Thermogravimetric analysis of calcium and lead hydroxylapatites and a series of their solid solutions prepared by precipitation from aqueous media reveal that the temperature-dependence of weight-loss was free from discontinuities up to 900° indicating that the water associated with the samples was not chemically bound. Simultaneous TGA and DTA traces of the end products have been used to study the thermal stabilities of the complexes. Presence of adsorbed water is indicated by thermoanalytical and IR studies.

WHILE the preparation of calcium hydroxylapatite  $[\text{CaHA}, 3\text{Ca}_3(\text{PO}_4)_2, \text{Ca}(\text{OH})_2]$ , lead hydroxylapatite (PbHA) and a series of their solid solutions by precipitation from aqueous media is described in detail<sup>1,2</sup>, thermal stabilities and the nature of water<sup>3-5</sup> associated with such samples need further clarification. We present here the results of thermoanalytical and IR studies on calcium and lead hydroxylapatites and their solid solutions.

The details of preparation of CaHA, PbHA and a series of their solid solutions have been described earlier<sup>2</sup>. Pasty masses of the samples obtained on centrifugation of their aqueous suspensions were air-dried, powdered and sieved through a 200 (BSS) mesh.

Thermogravimetric analysis of the samples (0.5 g) was carried out on a Stanton thermobalance adjusted to a temperature rise of 7-8°/min with a chart speed of 6 inch/hr. The heating was done up to 900° under dynamic conditions in air at atmospheric pressure, the partial pressure of water vapour being nearly constant. Simultaneous differential thermal analyses (DTA) and thermogravimetric analyses (TGA) of the end members, CaHA and PbHA, were carried out using a Mettler recording vacuum thermoanalyser. The derivative thermogravimetric (DTG) trace was also recorded in the case of CaHA. The IR spectra of the samples (heated previously to 900° for 6 hr and cooled *in vacuo*) and also of an air-dried sample of CaHA were recorded in the range 3800-700  $\text{cm}^{-1}$  (nujol) using a Perkin-Elmer double beam infrared spectrophotometer model 13U equipped with NaCl optics.

The thermal behaviour (TGA) of all the solid solutions of apatites was similar as far as the absence of discontinuities in the temperature-weight loss curves were concerned.

In the simultaneous TGA-DTA traces of CaHA and PbHA, for each sample there were two TGA

traces, TG<sub>1</sub> and TG<sub>2</sub>, of different sensitivities, the latter being more sensitive than the former. The zigzag nature of the DTA-TGA traces below 400° was found to be due to the instrumental fluctuations. Similar to the TGA patterns, TG<sub>1</sub> and TG<sub>2</sub> were found to be free from discontinuities up to 900°C. Endothermic peaks at 1460° and 960° in the DTA curves of CaHA and PbHA respectively suggest the onset of decomposition. The decomposition products of PbHA were volatile at temperatures higher than 1200° as revealed by a precipitous fall in the TGA traces while those of CaHA were found to be stable up to 1600°. No peak was observed in the DTG trace of CaHA.

It can be shown that during the process of dehydration, a hydrated sample constitutes a 3-phase system of the type, hydrate + dehydration product + water vapour. Being composed of two components such a system becomes univariant exhibiting discontinuities in its isobaric temperature-composition curves<sup>6</sup>. Each stage of such a dehydration has its characteristic heat of reaction depending upon the cleavage of linkages. On the other hand, the removal of water which is not chemically bound involves a 2-phase system of the type, solid + water vapour, resulting in bivariance for a 2-component system. The dissociation pressure of such a system is a continuous function of the composition leading to a continuous and uniform loss of water on dehydration. It is evident from the foregoing considerations that the water associated with the samples of apatites precipitated from aqueous media is not chemically bound. This conclusion is of significance in the light of the fact that  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$  are among the bivalent cations capable of forming aquo-cations of the type  $\text{M}(\text{H}_2\text{O})^{2+}$  (ref. 7).

In the light of the endothermic peaks observed in the DTA traces of the samples it can be concluded that 900° is a safe upper limit for heating the precipitated samples of apatites to drive out the adsorbed water without bringing about thermal decomposition and to facilitate the attainment of sharp Debye-Scherrer patterns of the samples.

The IR spectra of the apatites show the characteristic peaks of the orthophosphate ion in the range 1100-960  $\text{cm}^{-1}$ . In addition, the absence of peaks in the range 1450-1410  $\text{cm}^{-1}$  assignable to carbonate ion indicates the absence of carbonate apatite<sup>8</sup> which is a likely impurity in such samples. Further, the absence of peaks at 917, 1151 and 1152  $\text{cm}^{-1}$  confirms the absence of pyrophosphate ion suggesting that the heating of the samples at 900° did not decompose the samples since pyrophosphate is one of the products of thermal decomposition of orthophosphates. Earlier work<sup>9,10</sup> could not convincingly establish the utility of IR data in differentiating between the chemically bound and the adsorbed types of water. A band observed at 1635  $\text{cm}^{-1}$  in the IR spectra of air-dried samples of CaHA and PbHA was found to vanish when the samples were

heated to 900°. Since the thermoanalytical studies indicate that the water in apatites is not chemically bound, the peak at 1635 cm<sup>-1</sup> may be considered to be characteristic of adsorbed water.

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### Calcium Complex Grease as a Suitable Substrate for Gas Liquid Chromatography

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Calcium complex grease has been evaluated for its suitability as a stationary phase for GLC. It elutes symmetrical peaks within short time and can successfully be used up to 250° with negligible bleed. Qualitative and quantitative results are obtained with this grease for several test mixtures. Data on relative retention time for various solutes with respect to *n*-hexane are also reported.

CONSIDERABLE work has been done on solvent efficiency of a variety of greases used as stationary phase in gas liquid chromatography (GLC)<sup>1,2</sup>. Present investigation was undertaken to study the solvent efficiency of calcium complex grease in GLC.

The wheel bearing grease which is available in the market was used as a substrate for GLC columns. The physico-chemical properties were first examined. The general *n-d-M* methods<sup>3</sup> along with IR spectroscopy<sup>4</sup> revealed the presence of 80% petroleum oil as the fluid (paraffins 78%, aromatics 17% and naphthenes 5%) and 20% soap as the thickener (calcium acetate + calcium stearate). Thermal stability of the grease was examined by thermogravimetric analysis indicating a loss of 2% at 250° and 5% at 300°, beyond which the decomposition started. Therefore, it can be used up to 250° safely.

Three columns with different loading of the grease and with varying parameters were prepared and

used after conditioning them for 24 hr at 250° with nitrogen flow rate 80 ml/min. Beckman GC-2A gas chromatograph having thermal conductivity detector coupled with a Bristol 1 mV recorder was used. All the chemicals used were of extra pure quality (Polyscience Corporation, USA).

The behaviour of this phase, appeared satisfactory in terms of theoretical plate concept. Since the liquid phase must possess a solvent activity and should exhibit a differential solubility for solutes. The solvent efficiency of calcium complex grease on chromosorb 'W' 60/80 mesh, acid washed coiled stainless steel column (2 m × 4.5 mm) was determined for various compounds and the data are presented in Table 1.

Few standard mixtures were quantitatively evaluated on this phase by usual methods. The calculated values were in close agreement with the values known for standard mixtures. The elution curves from the calcium complex grease columns are sharp and symmetrical for diverse types of solutes. Separation of consecutive peaks can be measured from these chromatograms in terms of resolution<sup>5</sup>, which measures both the column and solvent efficiency. Some special features of this phase for practical purposes have been studied. Low coating of the phase in a short column exhibited fast analysis of high boiling compounds, indicating the possibilities of its usefulness in resolving higher members in a homologous series. Chromatograms recorded at 140° on a short column (1 m × 4.5 mm)

TABLE 1 — RETENTION DATA ON 10% CALCIUM COMPLEX GREASE

(Carrier gas, hydrogen; inlet pressure 17 psi; column temperature 100°)

Sl No.	Solutes	b.p., °C (760 mm)	Retention relative to <i>n</i> -hexane
1	<i>n</i> -Pentane	36.1	0.45
2	<i>n</i> -Hexane	68.7	1.00
3	<i>n</i> -Heptane	98.4	1.97
4	<i>n</i> -Octane	125.6	4.18
5	<i>n</i> -Decane	174.0	17.94
6	2,4,4-Trimethyl pentene-1	101.4	2.21
7	2,4,4-Trimethyl pentene-2	104.9	3.21
8	3,5,5-Trimethyl-1-hexene	—	7.71
9	Benzene	80.1	2.00
10	Toluene	110.6	4.29
11	Ethylbenzene	136.2	8.08
12	( <i>p</i> + <i>m</i> )-xylene	138.4	8.93
13	<i>o</i> -Xylene	144.4	10.71
14	Cumene	152.4	11.94
15	Mesitylene	164.7	18.71
16	Dichloromethane	40.0	0.64
17	Chloroform	61.0	1.43
18	Carbon tetrachloride	76.8	1.86
19	Ethyl acetate	77.2	0.79
20	Nitromethane	101.3	0.71
21	Pyridine	115.3	3.57
22	Methanol	64.7	0.21
23	Ethanol	78.5	0.34
24	Isopropanol	82.3	0.43
25	<i>n</i> -Propanol	97.2	0.73
26	Isobutanol	108.4	1.29
27	<i>n</i> -Butanol	117.7	1.71
28	Cyclohexane	80.7	1.71
29	Formaldehyde	—	0.21
30	Water	100.0	1.36
31	Acetone	56.5	1.43
32	Methyl ethyl ketone	79.6	0.86