SECTION II

PREPARATION AND CHARACTERIZATION OF
LEAD PHOSPHATE APATITE, LEAD VANADATE APATITE
AND
THEIR SOLID SOLUTIONS
PREPARATION AND CHARACTERIZATION OF LEAD PHOSPHATE
APATITE, LEAD VANADATE APATITE AND THEIR SOLID
SOLUTIONS.

2.1 Introduction

The toxicity of elemental lead and its compounds is well known. Their inhalation in the form of dust or fumes and absorption through the skin lead to "lead poisoning" (also known as "Plumbism") which is an occupational disease prevalent mostly among workers dealing with white-lead and pottery. The disease is characterised by symptoms such as anaemia, constipation, mental and visual disturbances and convulsions. Toxic effects caused by lead present in Mexican pottery were discussed recently by Gerald et al. Studies to explain the ultimate site and mechanism of incorporation of lead in the human metabolism are consequently of great pathological significance. An awareness of the hazards caused by lead is indicated by the fact that in the United Kingdom a legislation to permit the use of automobiles run on petrol freed from lead is being contemplated.

According to Klement the criterion facilitating the incorporation of lead in the human skeletal system is the formation of solid solutions of hydroxyl-apatites of calcium and lead, the factors contributing to
such a formation being the isomorphism existing between them and the closeness of the ionic radii of calcium and lead (0.99 and 1.20 Å respectively).

In the context of toxicity, vanadium does not lag very much behind lead, the principal toxic symptoms being paralysis, convulsions and sleepiness leading to bronchitis and bronchopneumonia. While the selective toxicity of vanadium in mammals is established its mechanism in living cells is still to be investigated. Apart from toxicity considerations, vanadium demands a detailed investigation by virtue of the role played by it in industries as a catalyst and in metallurgy as a principal ingredient in special varieties of steels.

Consequent upon the fact that tetrahedral $\text{VO}_4^{3-}$ ion and its isostructural $\text{PO}_4^{3-}$ ion have covalent radii close to one another, (1.22 and 1.10 Å respectively), the latter present in lead phosphate apatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, can be isomorphously replaced by the former leading to lead vanadate apatite (the two apatites being abbreviated hereafter as LPA and LVA respectively). While extensive work has been done on LPA, studies on its solid solution with LVA have not been undertaken. LVA being a compound containing both the potentially toxic elements, namely lead and vanadium,
investigations on such solid solutions are being considered to be extremely significant from the point of view of toxicity to human skeletal system and hence the present work was undertaken.

It was Klement\textsuperscript{83} who could successfully prepare LPA for the first time both by wet and dry methods. While hydrolysis of secondary lead phosphate could form LPA by a wet method, the same could be prepared by a dry method by subjecting a stoichiometric mixture of tertiary lead phosphate and lead oxide to an optimum temperature under a stream of moist air. Another wet method for preparation of LPA ensuring the elimination of coprecipitation of acid phosphate and hydroxide of lead was suggested by Rathje\textsuperscript{37,47} based on what is known as "acidimetric precipitation", a modification of the same being adopted by Müller.

Solutions of lead nitrate and potassium dihydrogen phosphate added simultaneously to boiling water maintained highly alkaline resulted in the formation of LPA, the coprecipitation of acid phosphate and hydroxide of lead being avoided by the presence of surplus potassium hydrogen phosphate in the medium of precipitation.

An alternative method suggested by Hayek\textsuperscript{45} to eliminate coprecipitation of lead was based on converting the latter into one of its soluble tartrate complexes in
an ammoniacal medium to be dissociated by heating when desired for preparation of LPA. While studies on LPA are extensive many aspects concerning LVA are still to be investigated. LVA needed specifically for X-ray analysis was prepared for the first time by Engel229 through hydrothermal synthesis.

The present investigations deal with preparation of LPA, LVA and a series of their solid solutions through a modified method of collins46, the samples so prepared being characterised through chemical, X-ray, i.r, electron-microscopic and thermogravimetric analyses. The method adopted is the first of its kind for preparation of LVA in appreciable quantities by precipitation.

2.2 Experimental

The experimental work included in this section has been subdivided into (i) Preparation, (ii) chemical analysis, (iii) determination of lattice constants, (iv) electronmicroscopic investigations, (v) i.r studies and (vi) Thermoanalytical studies of the samples.

2.2.1 Preparation of the Samples

The preparation of the samples of LPA, LVA and their solid solutions was based on the following equation:-
\[ 10 \text{Pb}^{2+} + 6 \times \text{O}_4^{2-} + 2 \text{OH}^- \rightarrow \text{Pb}_{10} \left( \text{XO}_4 \right) _6 \left( \text{OH} \right) _2 \]

where \( \text{X} = \text{P} \) or \( \text{V} \) for the end-members and \( (\text{P}+\text{V}) \) for the solid solutions, the proportion of \( \text{P} \) to \( \text{V} \) being varied as desired. The samples were precipitated at 37°C by mixing stoichiometric quantities of the reactants in the form of their aqueous solutions maintained at a \( \text{pH} \) of 12. The precipitation was done in an atmosphere freed from carbon dioxide and the chemicals used were of L.R. grade. All the solutions were prepared in water freed from carbon dioxide. Based on the above equation, calculated amounts of lead acetate, diammonium hydrogen phosphate and sodium ortho vanadate were taken such that the yield was about 30 g of the sample. Ethylene diamine was used instead of ammonia since relatively smaller volumes of it were required to maintain the reacting solutions at the desired \( \text{pH} \). In addition, the unpleasant smell of ammonia could be avoided. The desired solutions were prepared as described below:

**Solution A.**

Approximately 1M lead acetate solution, this was prepared by dissolving about 380 g of lead acetate, \( \text{Pb} \left( \text{CH}_3\text{COO} \right) _2 \cdot 2\text{H}_2\text{O} \), in water and making up the volume to 1 litre, its lead content being determined complexometrically. A desired volume of this solution was
added dropwise under constant stirring to an appropriate volume of ethylene diamine, determined previously by a trial experiment, such that the solution maintained a pH of 12 on making up to 1000 ml. Since the addition of ethylene diamine to lead acetate solution resulted in precipitation, probably of lead hydroxide, care was taken to see that mixing was done in the reverse way such that the surplus concentration of ethylene diamine facilitated the retention of lead in the form of a soluble complex. This was taken in a 3 necked round-bottomed flask of 3 litre capacity.

Solution B.

Approximately 0.5M solution of diammonium hydrogen phosphate. This was prepared by dissolving approximately 70 g of diammonium hydrogen phosphate in water and making up the volume to 1 litre, its phosphorus content being determined by Washburn and Shear's method.

Solution C.

Approximately 0.5M Sodium ortho vanadate solution. A sample of Ammonium meta vanadate was subjected to heating at \( \sim 400^\circ C \) for \( \sim 4 \) hours to convert it into vanadium pentoxide. About 50 g of the resulting sample were dissolved in 2N sodium hydroxide solution such that the total volume
was 1 litre, the vanadium content of the solution being determined iodimetrically.

An appropriate volume of Solution 'B' or 'C' or a mixture of them which was in a stoichiometric proportion to that of Solution 'A' was treated with a predetermined volume of ethylene-diamine such that it maintained a pH of 12 on making up to 1 litre and taken in a dropping funnel. The funnel was closed by a hollow ground - glass stopper, connected to soda-lime towers and fitted into a quick-fit socket of a 3-necked flask of 3 litre capacity containing solution A maintained at 37°C. While the solution from the dropping funnel was drained drop by drop, CO₂-free air obtained by the use of soda-lime towers and water suction pump was bubbled through the solution 'A' to eliminate the formation of carbonate-apatite and to keep it, in addition, well stirred. The precipitate was refluxed for about two hours in contact with the mother liquor, left overnight, filtered through a 104 sintered glass crucible, washed till washings were neutral and air dried. A part of it was heated to ~300°C for ~6 hours, for purposes of X-ray diffraction studies. A schematic representation of the assembly of the apparatus used for the preparation of the samples was given in Figure 2.1
Fig. 2-1 Assembly of the apparatus used for the preparation of Lead Phosphate, apatite, Lead Vanadate apatite and their solid solutions.
2.2.2 Chemical Analyses

The chemical analysis of LPA is complicated by the mutual interference of lead and phosphate ions and consequently special analytical techniques are desired for the purpose. In presence of vanadate ions these complications become more pronounced as in the case of solid solutions of LPA and LVA. Although instrumental methods of analysis such as spectrophotometry\textsuperscript{69}, x-ray fluorescence\textsuperscript{46} and flame photometry\textsuperscript{232} have frequently been used for such determinations, they have a limited range of applicability. The desirability to special analytical techniques to bring about quantitative separation of these ions was therefore felt. When once such a separation was achieved, complexometric titrations\textsuperscript{68} were found to be suitable for the subsequent determinations.

While for the end-embers Pb\textsuperscript{2+} is to be quantitatively separated from either PO\textsubscript{4}\textsuperscript{3-} or VO\textsubscript{4}\textsuperscript{3-} ions, for the solid solutions all the three ions are to be separated from one another. The accuracies of the procedures adopted were assessed by analysing sample solutions containing known quantities of the respective ions. The solutions used for these determinations were prepared in double-distilled water tested previously for the likely ions that
interfere in the subsequent complexometric determinations and preserved in polyethylene containers.

From an aliquot of a solution containing the three ions Pb\(^{2+}\) and PO\(_4^{3-}\) were determined gravimetrically as Pb(10\(_3\))\(_2\)\(^{233}\) and MgNH\(_4\)PO\(_4\).6H\(_2\)O\(^{67}\) respectively. From another aliquot, reducing vanadium from +5 to +4 state using hydrazine hydrate, the combined amount of Pb\(^{2+}\) and V\(_2\)O\(_7^{2+}\) was determined complexometrically\(^{234}\) from which subtraction of Pb content determined earlier gave that of vanadium.

The following solutions were prepared for the purpose

(a) Standard 0.01M EDTA Solution.

The disodium salt of EDTA (ethylene diamine tetraacetic acid) was dried for about 12 h at 80°C and cooled in a desiccated atmosphere so that the compound attained the composition of its dihydrate, Na\(_2\)H\(_2\)C\(_{10}\)H\(_{12}\)O\(_8\)N\(_2\).2H\(_2\)O. 1 litre of 0.01M EDTA solution contained 3.7224 g of this dried substance.

(b) Lead Nitrate solution containing 1 mg of Pb per ml.

It was prepared by dissolving 1.0038 g of metallic lead in nitric acid (Sp. gr. 1.42) and the solution was evaporated to dryness. The mass was extracted with distilled
water and the volume made up to 1 litre. The lead content of the solution was determined complexometrically using Xylenol-orange as indicator at a pH of ~5 obtained by hexamine as buffer.

(e) Potassium Dihydrogen Phosphate solution containing 1 mg of P per ml: 4.3930 g of $\text{KH}_2\text{PO}_4$ heated previously to constant weight at $110^\circ\text{C}$ were dissolved and made up to 1 litre.

(d) Sodium orthovanadate Solution containing 1 mg of 'V' per ml. Ammonium meta vanadate was heated to ~400°C for ~4 hrs and a convenient amount of the resulting $\text{V}_2\text{O}_5$ was dissolved in approximately 2N sodium hydroxide solution and made up to 500 ml using the same solution. Knowing the vanadium content of the resulting solution iodimetrically a required volume of it was measured accurately such that on making it up to 1 litre using ~2 N sodium hydroxide the resulting solution contained 1 mg of $\text{V}$ per ml.

In addition, (e), 0.5% solution of Xylenol orange and (f) approximately 6% solution of potassium iodate were prepared.

2.2.2.1 Quantitative Separation of $\text{Pb}^{2+}$ and $\text{PO}_4^{3-}$ ions.

From standard stock solutions of lead and
phosphorus (solutions 'b' and 'c' mentioned above)
convenient volumes were mixed and the resulting solution
was subjected to a quantitative separation of these
elements by the following procedure to assess the accuracy
of the method adopted.

The solution was made distinctly acidic by
adding nitric acid (sp. gr. 1.42), heated to boiling,
treated with ~30 ml of ~6 per cent potassium iodate
solution under constant stirring and then maintained at
~70°C for ~30 minutes cooled and filtered through
1G3 sintered glass crucible. The residue was washed
repeatedly using small portions of a total ~75 ml of
0.2 per cent potassium iodate solution prepared in
1 percent nitric acid. It was followed by washing
successively with three 2 ml portions of ice-cold water
and finally twice with a little dry acetone; the washings
throughout the above operations being added to the filtrate.
The crucible was dried to constant weight at 140°C and
weighed as Pb (10\textsubscript{3})\textsubscript{2}.

From the filtrate Mg NH\textsubscript{4}PO\textsubscript{4}·6H\textsubscript{2}O was precipitated
by treating it with 2 drops of methyl red indicator and
an excess of 0.5N magnesium chloride solution, followed by
the addition of ~9 M ammonium hydroxide till the solution
turned colourless, the presence of excess of Mg\textsuperscript{2+} being confirmed by the absence of further precipitation from the supernatant liquid on addition of the precipitant. It was left overnight in contact with the mother liquor, filtered through a 164 sintered glass crucible, washed successively with \textapprox 0.4 M ammonium hydroxide, acid-free alcohol and ether till freed from the accompanying ions, dried overnight to constant weight at 37\textdegree C and weighed as Mg NH\textsubscript{4} PO\textsubscript{4} \textcdot 6H\textsubscript{2}O.

2.2.2.2 A Quantitative Separation of Pb\textsuperscript{2+} and VO\textsubscript{4}\textsuperscript{3-} ions.

From standard stock solutions of lead and vanadium (solutions 'b' and 'd' mentioned above), convenient volumes were mixed and the resulting solution was subjected to quantitative separation of the elements by the following procedure to assess the accuracy of the method adopted.

From an aliquot of this mixture lead was determined as Pb(10\textsubscript{3})\textsuperscript{2} as in 2.2.2.1, while from another a combined estimation of it with vanadium was made in the following manner to get the amount of the latter. The solution was treated with \textapprox 10 ml of \textapprox 6 M hydrochloric acid and 2 ml of hydrazine hydrate, heated to boiling on a water bath to reduce vanadium from +5 to +4 state, cooled to room temperature and treated with a known volume of standard
solution of 0.01 M EDTA taking care to see that it was more than what was required, the pH being brought to
\( \sim 3 \) by adding 2N \( \text{NaOH} \) solution followed by the addition of 3 drops of Xylenol orange to be used as indicator.
The attainment of the required pH (\(~5\)) was ensured by the addition of \( \sim 1 \text{ g} \) of hexamine (hexamethylene tetramine). The excess EDTA was back-titrated with a standard 0.005M lead nitrate solution, the colour change being from yellow to red.

2.2.2.3 A Quantitative Separation of \( \text{Pb}^{2+} \), \( \text{PO}_4^{3-} \) and \( \text{VO}_4^{3-} \) ions—It is evident that a combination of methods given under 2.2.2.1 and 2.2.2.2 when applied in succession to a solution containing \( \text{Pb}^{2+} \), \( \text{PO}_4^{3-} \) and \( \text{VO}_4^{3-} \) could enable a quantitative separation of all the three ions to be made.

The above methods were applied to the chemical analyses of LPA, LVA and their solid solutions, convenient amount of each being dissolved in a minimum quantity of 4N Nitric acid and made up to 500 ml.

2.2.3 Determination of unit-cell volumes—The criteria for a given pair of substances to form solid solutions are that the two substances are isomorphous and the ionic radii of the corresponding pairs of ions are comparable. It is
evident that LPA and LVA fulfil these requirements. Since the replacement of $PO_4^{3-}$ by $VO_4^{3-}$ (covalent radii 1.10 and 1.22 Å respectively) in an apatite lattice brings about a dilation of the unit cell, a proof for the formation and homogeneity of the resulting solid solutions can be provided by the determination of the lattice constants and the accompanying calculation of the unit cell volumes. The Debye-Scherrer powder method was found to be suitable for the purpose, since the samples are microcrystalline in nature being precipitated from aqueous media. The samples subjected to these investigations were previously heated for ~ 6 h at ~300°C in order to increase the size of the crystals so that the sharpness of the diffraction lines could be enhanced. The patterns of the samples (Nos. 1, 2, 3 and 8 of Table 2.5 P) were recorded using a Debye-Scherrer camera of 114.6 cm diameter with a rotating-sample exposed to Cu $K_\alpha$ radiation, the voltage, current strength and exposure time being 40KV, 25 mA and 5 h while those of other samples (Nos. 4, 5, 6 and 7 of Table 2.5 P) were recorded using Co radiation, voltage, current strength and exposure time being 20 KV, 5 mA and 40 h. The distance between each line on the pattern and the point where the transmitted beam would strike the film in the absence of diffraction was measured using a micrometer scale.
from which values of 2θ and d were calculated. Using statistical methods, the lines corresponding to about 10 reflection planes were indexed for each sample.

2.2.4 Electronmicroscopic investigations

The conclusions drawn from x-ray diffraction patterns confirming the homogeneity of the samples could be supplemented by their electron micrographs which, in addition, could scrutinise the absence of extraneous phases and provide visual information about the geometry and dimensions of the individual crystals of the samples. Air-dried samples were found to be better suited for the purpose than those heated to 300°C, since the latter operation was found to lead to fusion of the individual crystals into large crystalline masses preventing thereby the measurement of the dimensions of individual crystals.

A pinch of the sample was dispersed in a few ml of water and the suspension was subjected for a few minutes to ultrasonic radiation at a frequency of a few hundred kilocycles per sec. in order to break down the conglomeration of the individual crystals. A drop of the resulting slurry was taken on a copper grid, placed in the vacuum chamber of an electron microscope (Philips, EM 300) with carbon
as back-ground and the specimen exposed to the electron beam after evacuation, the resulting image being viewed on a small fluorescent screen. When the field of vision consisted of well defined individual crystals, it was photographed. From each electron micrograph, a few individual crystals, preferably of varying dimensions, were focussed at random under a calibrated eye-piece and through measurement of the length and breadth of these crystals their average dimensions were calculated. An attempt was made to calculate the specific surface areas of a few representative samples among those prepared using the measured length and breadth. The crystals of the samples which are in the form of elongated hexagonal prisms could be considered as cylinders \( 237 \) for purposes of evaluation of their approximate specific surface areas using the expression,

\[
\frac{2 \pi r^2 + 2 \pi rh}{\pi r^2 h \phi}
\]

where \( r = 0.5 \) times the average breadth, \( h = \) average length, \( \phi = \) density of the sample.

It is evident that the rates of dissolution \( 110 \) of the samples which decide the period of equilibration required for the attainment of saturation are dependent on their surface areas. In addition the utility of apatites as luminescent phosphors and ion-exchangers \( 117 \) is also
controlled by their surface areas. An evaluation of the surface areas of the samples is therefore justified.

2.2.5 Infrared Spectra

The infrared absorption spectra of the samples were recorded as nujol mulls using a Perkin Elmer Infrared Spectrophotometer, Model 297, equipped with KBr optics. The spectra were recorded within a wave-number range of 4000-650 cm\(^{-1}\). The operation of the instrument was based on directing alternatively the i.r. radiation through the test and reference samples and bringing together the two transmitted beams on a thermo-couple. With unequal absorption in the two paths a pulsating output was generated, amplified and made to operate a variable shutter to increase or decrease the intensity of the reference beam which could then be recorded on a chart paper as a function of the wave number. In addition to the patterns recorded as nujol mulls, those using KBr pellets were also recorded in the case of the end-numbers.

2.2.6 Thermoanalytical Studies

Thermogravimetric analyses of the samples were intended to know their thermal stabilities with special reference to the removal of volatile impurities, the nature
of water associated with the samples and the decomposition
 temperatures. It may be mentioned that there is no earlier
 literature available on thermoanalytical studies of LPA
 and LVA. These investigations were restricted exclusively
to the two end-members, LPA and LVA, and not extended to
their solid solutions since the earlier investigations on
allied system indicated that the solid solutions exhibited
a behaviour intermediary to that of the end-members.

A convenient weight of the sample (about 0.5g)
was taken in a 10 ml capacity platinum crucible and
suspended from the pan of a micro-balance, the crucible
being housed in a high temperature furnace (F.C.I., Sindri,
India). Starting from ambient temperature, the sample was
heated at a convenient rate (\(-8^\circ\text{C} / \text{min.}\)) up to a maximum
of about 900\(^{\circ}\text{C}\). At frequent intervals the weight of the
sample and the corresponding furnace temperature were
recorded so that the dependence of per cent weight loss
on temperature could be represented.
### Table 2-1
Quantitative separation of lead and phosphorus - Assessment of Attainable accuracy

<table>
<thead>
<tr>
<th>Element</th>
<th>I</th>
<th>II</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theo.</td>
<td>Expnl.</td>
<td>% Error</td>
<td>Theo.</td>
</tr>
<tr>
<td>Lead</td>
<td>27.47</td>
<td>27.33</td>
<td>-0.50</td>
<td>33.00</td>
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<tr>
<td>Phosphorus</td>
<td>10.00</td>
<td>9.96</td>
<td>-0.40</td>
<td>70.00</td>
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### Table 2-2
Quantitative separation of lead and vanadium - Assessment of attainable accuracy

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theo.</td>
<td>Expnl.</td>
<td>% Error</td>
<td>Theo.</td>
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<td>Lead</td>
<td>54.70</td>
<td>54.80</td>
<td>-0.20</td>
<td>33.00</td>
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<tr>
<td>Vanadium</td>
<td>10.00</td>
<td>9.90</td>
<td>+1.00</td>
<td>12.00</td>
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Table 2-3
Quantitative separation of lead, phosphorus and vanadium - Assessment of attainable accuracy

<table>
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<th>Trial No.</th>
<th>Lead</th>
<th>Phosphorus</th>
<th>Vanadium</th>
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<tr>
<td>1</td>
<td>49.10</td>
<td>49.30</td>
<td>+0.40</td>
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<tr>
<td>2</td>
<td>39.30</td>
<td>38.80</td>
<td>-1.30</td>
</tr>
<tr>
<td>3</td>
<td>29.50</td>
<td>29.40</td>
<td>-0.30</td>
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Table 2.4

Determination of g atom ratio \( \frac{Pb}{(P+V)} \), of phosphate and vanadate apatites of lead and their solid solutions

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sample</th>
<th>Pb (3)</th>
<th>P (4)</th>
<th>V (5)</th>
<th>Molecular formula*</th>
<th>g atom ratio, ( \frac{Pb}{(P+V)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Lead phosphate apatite (LPA)</td>
<td>77.86</td>
<td>6.97</td>
<td>-</td>
<td>( Pb_{10}(PO_4)_6(OH)_2 )</td>
<td>1.67</td>
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<tr>
<td>2.</td>
<td>Solid Solution I</td>
<td>76.61</td>
<td>6.19</td>
<td>1.16</td>
<td>( Pb_{10}(PO_4)<em>{5.4}(VO_4)</em>{0.6}(OH)_2 )</td>
<td>1.66</td>
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<td>3.</td>
<td>II</td>
<td>77.36</td>
<td>5.13</td>
<td>2.74</td>
<td>( Pb_{10}(PO_4)<em>{4.5}(VO_4)</em>{1.5}(OH)_2 )</td>
<td>1.70</td>
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<tr>
<td>4.</td>
<td>III</td>
<td>76.69</td>
<td>4.15</td>
<td>4.22</td>
<td>( Pb_{10}(PO_4)<em>{3.69}(VO_4)</em>{2.31}(OH)_2 )</td>
<td>1.71</td>
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<td>5.</td>
<td>IV</td>
<td>75.61</td>
<td>3.37</td>
<td>5.55</td>
<td>( Pb_{10}(PO_4)<em>{3}(VO_4)</em>{3}(OH)_2 )</td>
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<td>6.</td>
<td>V</td>
<td>75.46</td>
<td>2.99</td>
<td>6.40</td>
<td>( Pb_{10}(PO_4)<em>{2.6}(VO_4)</em>{3.4}(OH)_2 )</td>
<td>1.64</td>
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<td>7.</td>
<td>VI</td>
<td>75.26</td>
<td>2.15</td>
<td>7.54</td>
<td>( Pb_{10}(PO_4)<em>{1.9}(VO_4)</em>{4.1}(OH)_2 )</td>
<td>1.67</td>
</tr>
<tr>
<td>8.</td>
<td>VII</td>
<td>75.69</td>
<td>1.32</td>
<td>8.81</td>
<td>( Pb_{10}(PO_4)<em>{1.2}(VO_4)</em>{4.8}(OH)_2 )</td>
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<td>9.</td>
<td>VIII</td>
<td>75.24</td>
<td>0.45</td>
<td>10.42</td>
<td>( Pb_{10}(PO_4)<em>{0.4}(VO_4)</em>{5.6}(OH)_2 )</td>
<td>1.66</td>
</tr>
<tr>
<td>10.</td>
<td>Lead vanadate apatite (LVA)</td>
<td>74.37</td>
<td>-</td>
<td>10.80</td>
<td>( Pb_{10}(VO_4)_6(OH)_2 )</td>
<td>1.69</td>
</tr>
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</table>

* Based exclusively on Pb, P and V contents, (OH) content being assumed to be stoichiometric.
Table 2.5
Lattice Constants and Unit Cell Volumes of Phosphate and Vanadate apatites of Lead and a few of their solid solutions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Lattice Constants (Å)</th>
<th>C/a</th>
<th>Unit Cell Volume (Å³)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
<td>c/n</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Direct Refined*</td>
<td>Direct Refined*</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(4)</td>
<td>(5)</td>
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<td></td>
<td>(10)</td>
<td>(11)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Pb₁₀(PO₄)₆(OH)₂</td>
<td>2675.8</td>
<td>9.889</td>
<td>9.8877</td>
<td>7.485</td>
</tr>
<tr>
<td>2</td>
<td>Pb₁₀(PO₄)₅.₄(VO₄)₀.₆(OH)₂</td>
<td>2687.9</td>
<td>9.910</td>
<td>9.9172</td>
<td>7.460</td>
</tr>
<tr>
<td>3</td>
<td>Pb₁₀(PO₄)₄.₅(VO₄)₁.₂(OH)₂</td>
<td>2705.7</td>
<td>9.970</td>
<td>9.9614</td>
<td>7.453</td>
</tr>
<tr>
<td>4</td>
<td>Pb₁₀(PO₄)₃.₆₉(VO₄)₂.₃₁(OH)₂</td>
<td>2721.9</td>
<td>9.977</td>
<td>9.9997</td>
<td>7.458</td>
</tr>
<tr>
<td>5</td>
<td>Pb₁₀(PO₄)₂.₆(VO₄)₃.₄(OH)₂</td>
<td>2743.6</td>
<td>10.065</td>
<td>10.0557</td>
<td>7.438</td>
</tr>
<tr>
<td>6</td>
<td>Pb₁₀(PO₄)₁.₉(VO₄)₄.₁(OH)₂</td>
<td>2757.7</td>
<td>10.117</td>
<td>10.0911</td>
<td>7.417</td>
</tr>
<tr>
<td>7</td>
<td>Pb₁₀(PO₄)₁.₂(VO₄)₄.₈(OH)₂</td>
<td>2771.6</td>
<td>10.128</td>
<td>10.1235</td>
<td>7.476</td>
</tr>
<tr>
<td>8</td>
<td>Pb₁₀(VO₄)₆(OH)₂</td>
<td>2795.5</td>
<td>10.163</td>
<td>10.1825</td>
<td>7.447</td>
</tr>
</tbody>
</table>

*Lattice parameters were refined by the method of least squares using a micro computer and hence are given up to four places of decimal.
Table 2-6

Approximate dimensions of individual crystals and specific surface areas of phosphate and vanadate apatites of lead and of a representative solid solution.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Density (g/ml)</th>
<th>Average dimensions of individual crystals (Å)</th>
<th>Approximate surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Length</td>
<td>Breadth</td>
</tr>
<tr>
<td>A</td>
<td>Lead Phosphate apatite</td>
<td>6.980</td>
<td>2512</td>
<td>1012</td>
</tr>
<tr>
<td>B</td>
<td>Solid Solution (80% LVA)</td>
<td>7.081</td>
<td>2303</td>
<td>744</td>
</tr>
<tr>
<td>C</td>
<td>Lead vanadate apatite</td>
<td>7.112</td>
<td>2625</td>
<td>1062</td>
</tr>
<tr>
<td>S. No.</td>
<td>Molecular formula</td>
<td>$\text{PbO}_4$</td>
<td>$\text{VO}_4$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>-------</td>
<td>-------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>1</td>
<td>$\text{Pb}_{10}\left(\text{PO}_4\right)_6(\text{OH})_2$</td>
<td>$1040,975$</td>
<td>$520,570,920-1050^*$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{5.4}(\text{VO}<em>4)</em>{0.6}(\text{OH})_2$</td>
<td>$1040,980$</td>
<td>$780$</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{4.5}(\text{VO}<em>4)</em>{1.5}(\text{OH})_2$</td>
<td>$1040,980$</td>
<td>$780,760$</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{3.69}(\text{VO}<em>4)</em>{2.31}(\text{OH})_2$</td>
<td>$1050,980$</td>
<td>$800,750$</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{3}(\text{VO}_4)_3(\text{OH})_2$</td>
<td>$1050,980$</td>
<td>$800,750$</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{2.6}(\text{VO}_4)_3.4(\text{OH})_2$</td>
<td>$1050,980$</td>
<td>$800,750$</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{1.9}(\text{VO}_4)_4.1(\text{OH})_2$</td>
<td>$1050,1020,980$</td>
<td>$810,750$</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{1.2}(\text{VO}_4)_4.8(\text{OH})_2$</td>
<td>$1050,965$</td>
<td>$800,750$</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>$\text{Pb}_{10}\left(\text{PO}<em>4\right)</em>{0.4}(\text{VO}_4)_5.6(\text{OH})_2$</td>
<td>$1025$</td>
<td>$800,735$</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>$\text{Pb}_{10}(\text{VO}_4)_6(\text{OH})_2$</td>
<td>-</td>
<td>$840,800,740$</td>
<td>-</td>
</tr>
</tbody>
</table>

* Determined with the sample as KBr pellet while the rest were as mull mulls.
Fig. 2-2  Debye-Scherrer diffraction powder patterns of samples (S.Nos. 1, 2, 3 and 4, Table 2-5.)

1. Lead phosphate apatite
2. Solid Solution No. 1 (10.0 mole % Lead Vanadate apatite).
3. Solid Solution No. 2 (25.0 % mole % Lead Vanadate apatite).
4. Solid Solution No. 3 (38.0 mole % Lead Vanadate apatite).
Fig. 2-3 Debye - Scherrer diffraction powder patterns of samples (S.No.s 5, 6, 7 and 8, Table 2.5).

5. Solid Solution No. 4 (57.0 mole % Lead Vanadate apatite).
6. Solid Solution No. 5 (69.0 mole % Lead Vanadate apatite).
7. Solid Solution No. 6 (80.0 mole % Lead Vanadate apatite).
8. Lead Vanadate apatite.
Fig. 2.4 (I) Dependence of lattice Constants \( \frac{c}{a} \) of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent of Lead Vanadate apatite (Column 4 and 6 of Table 2.5)

(II) Dependence of the ratio of the lattice Constants \( \frac{c}{a} \) of the solid solutions on the mole per cent of Lead Vanadate apatite. (Column 8 of Table 2.5)

(III) Dependence of unit cell volumes of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent of Lead Vanadate apatite. (Column 10 of Table 2.5)
Fig. 2-5 (I) Dependence of lattice constants of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent. of Lead Vanadate apatite.

(Taken from Column 5 and 7 of Table 2.5)

(II) Dependence of the ratio of lattice constants (c/a) of the solid solutions on the mole per cent. of Lead Vanadate apatite.

(Taken from column 9 of Table 2.5)
Fig. 2.6 Dependence of unit cell volumes of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent. of Lead Vanadate apatite.
(Taken from column 11 of Table 2.5)
Fig. 2-7  Electronmicrographs of the samples
   (S.Nos. A, B and C, Table 2.6)

(A) Electronmicrograph of Lead Phosphate apatite.

(B) Electronmicrograph of solid solution No. 6
    (80.0 mole per cent. of Lead Vanadate apatite).

(C) Electronmicrograph of Lead Vanadate apatite.

(magnification in all cases, 80,000 x ).
Fig. 2-8  I.R. traces of samples
(S.Nos. 1, 2 and 3, Table 2.7)

(1) Lead phosphate apatite

(2) Solid solution No.1 (10.0 mole %
Lead Vanadate apatite)

(3) Solid Solution No.2 (25.0 mole %
Lead Vanadate apatite).
Fig. 2.9 I.R. traces of samples
(5.Nos. 4,5 and 6, Table 2.7)

(4) Solid Solution No.3 (38.0 mole %
Lead Vanadate apatite)

(5) Solid Solution No.4 ( 50.0 mole %
Lead Vanadate apatite).

(6) Solid solution No.5 (57.0 mole %
Lead Vanadate apatite).
Fig. 2-10 I.R. traces of samples
(S.Nos. 7 and 8, Table 2.7).

(7) Solid Solution No. 6 (69.0 mole % Lead Vanadate apatite)

(8) Solid solution No. 6 (80.0 mole % Lead Vanadate apatite)
Fig. 2.11 I.R. traces of samples
(S Nos. 9 and 10, Table 2.7)

(9) Solid solution No. 7 (94.0 mole % Lead Vanadate apatite).

(10) Lead Vanadate apatite.
Fig. 2-12  I.R. traces of samples taken as KBr pellets

(1) Lead Phosphate apatite
(2) Lead Vanadate apatite.
2.3 Results

The accuracies of the methods employed for the chemical analyses of LPA, LVA and their solid solutions were scrutinised by applying these methods for analysis of sample solutions containing accurately weighed quantities of the ions concerned and the results were given in Tables 2.1 to 2.3, pp. ........ The analyses were conducted in each case with a set of three different concentrations. The ranges of errors expressed as weight per cents were found to be +0.40 to -1.30, 0.00 to -0.80 and -1.00 to 0.73 respectively, for lead, phosphorus and vanadium when present together.

Determination of the weight per cents of lead, phosphorus and vanadium of each one of the samples, arranged serially in Table 2.4 p. ........ in increasing order of vanadium content, was made and the results were given in columns (3), (4) and (5) of the Table. It is evident that for the samples the g atoms of phosphorus and vanadium present in 100 g of the sample can be calculated by dividing the respective percentages by the corresponding atomic weights. It is obvious that this ratio, P/V, is independent of the amount of the sample considered. Since the total number of g atoms of (P+V) in a mole of each sample is six,
knowing this ratio, the number of g atoms of Pb and V
in a mole of each sample could be calculated and the
molecular formulae of the samples indicated in column (6)
assigned assuming the number of lead and hydroxyl ions
to remain stoichiometric for the entire series of samples.
In addition, the g atom ratio, \( \frac{Pb}{(P+V)} \), was calculated for each
sample from the corresponding weight per cents and included
in column (7) of the Table; the ratio was found to vary
between 1.64 and 1.71, the theoretical value being 1.67.

Figs. 2.1 and 2.2, pp. ........... are the
Debye-Scherrer powder patterns of a few representative
samples and the data obtained from them were given in
Table 2.5, p. ....... The patterns are distinctly similar
as far as the distribution of the diffraction lines is
concerned, a uniform shift in the positions of corresponding
lines with increasing proportion of V-content being observed.
About ten well-defined lines were chosen from each one of the
patterns and their \( d \)-values were measured from which the
corresponding \( g \) values were calculated from the Bragg
equation. While cards 238, 239 containing hkl values
corresponding to different 'd' values are available for
the end-members, charts were used in the case of solid
solutions. The lattice parameters in all the cases were
calculated by a statistical method using the equations
given below:

\[ \sum x^2 + \beta \sum xy = \sum xz \quad \ldots \ldots \ldots \quad (2.i) \]

\[ \sum xy + \beta \sum y^2 = \sum yz \quad \ldots \ldots \ldots \quad (2.ii) \]

where

\[ \lambda = \frac{2}{3a^2}, \quad \frac{2}{4c^2} \]

\( \lambda \) = wave length of incident radiation used,

\[ x = h^2 + hk + k^2; \quad y = l^2 \quad \text{and} \quad z = \sin^2 \theta. \]

Values for 'a' and 'c' as well as for unit cell volumes were calculated by solving the above equations for \( \lambda \) and \( \beta \) and given in columns (4), (6) and (10) of the Table 2.5.

A refinement of these values was brought about by the method of least squares using a microcomputer, the new set of values being given in columns (5), (7) and (11) of the Table. The assigned molecular formulae and the corresponding molecular weights of the samples were given in column (2) and (3) of the Table. A graphical representation of the dependence of 'a' and 'c' and the unit cell volume on the mole per cent composition of the samples was provided by Figs 2.3(A) and 2.3(B) pp..........

The electronmicrographs of LPA, LVA and a representative solid solution of them were shown in Fig.2.4, p.... It is evident from these patterns that the crystals of the samples which existed individually or in clusters were mostly tabular or ribbon-like in shape
tending to look like elongated flattened hexagonal prisms. Based on the identity of the shape of the individual crystals evidence for the absence of phases other than that of apatites could be obtained confirming thereby the homogeneity of the samples. The average length and breadth and the approximate specific surface area calculated from them by assuming the hexagonals to be cylinders were given in Table 2.6.

The infra-red absorption spectra of the samples were given in Figs 2.5 to 2.8 pp. The wave number range investigated extended from 4000 - 650 cm\(^{-1}\) and the percentage transmittance or absorbance was represented as a function of the wave number of the radiation. It is evident that the absorption at 2920, 1460, 1375 cm\(^{-1}\) observed in all the patterns were of nujol. A consolidated list of absorption peaks of the samples assigned to \(\text{PO}_4^{3-}\), \(\text{VO}_4^{3-}\) and \(\text{OH}^-\) was given in Table 2.7, p. .... The i.r patterns of the end-members were found to contain the characteristic peaks of \(\text{OH}^-\) at 3540 cm\(^{-1}\) in addition to those of either \(\text{PO}_4^{3-}\) at 1040 and 980 cm\(^{-1}\) or \(\text{VO}_4^{3-}\) at 800 - 735 cm\(^{-1}\). The patterns of the solid solutions contained the entire set of these peaks. As expected, the intensity of the \(\text{VO}_4^{3-}\) peak increased while that of \(\text{PO}_4^{3-}\) diminished as the proportion of LVA in the samples increased. A systematic shift observed in these peaks over the entire compositional range of the solid solutions could be utilised as a criterion
for the homogeneity of the samples.

Thermogravimetric results on two representative samples, LPA and LVA, were carried out to arrive qualitatively at a suitable temperature below which alone the samples were to be heated for driving out volatile impurities. The results could show that discontinuity in the thermograms were absent up to 300°C suggesting this to be the temperature desired. However, more systematic and refined studies to establish the nature of water associated with them were to be undertaken later.
2.4 DISCUSSION

2.4.1 General Aspects

A brief mention of the theoretical aspects of solid solutions \(240,241\) was considered relevant here since the results included in this section were mainly concerned with them. Homogeneous crystals containing variable proportions of isomorphous substances* are formed, in general, from mixture of solutions of the end-members. These are consequently known as mixed crystals or more popularly as "solid solutions". A series of solid solutions can be extended to the entire or partial miscibility of the solids concerned. Solid solutions can be classified as interstitial and substitutional types. Interstitial solid solutions are those in which atoms of one element are inserted into some of the interstices in the crystal lattice formed by the atoms of a second element resulting usually in a small increase in lattice constants of the crystal. On the other hand substitutional solid solutions are those in which the replacement of atoms of one kind in the crystal lattice by atoms of a second kind with nearly the same size takes place.

The formation of substitutional solid solutions is accompanied either by an increase or a decrease in the unit cell volume depending upon the size of the substituent replaced. In general,

*The formation of solid solutions sometimes extends to a pair of solids belonging to dissimilar crystallographic types; the permissible range of compositions in such cases is limited and the products are known as "anomalous mixed crystals".
the ionic radii of a pair of ions competing for a given lattice position of the solid solution should not differ by more than about 15 per cent. Replacement of an ion by one or more ions of a different charge is also possible provided a charge neutrality is maintained. Such a replacement evidently results in a nonstoichiometric solid solution. A convincing proof for the formation of solid solutions can be provided by Vegard's law which states that a continuous series of solid solutions is characterised by a linear dependence of unit cell volume on the composition. Co-precipitation from solutions containing the required ions and crystallisation from molten mixtures of the end-members are the methods usually adopted for the preparation of solid solutions.

It has been established through X-ray diffraction techniques that LPA and LVA constituted a pair of isomorphous substances. The closeness of the covalent radii of P (1.10 Å) and V (1.22Å) suggests the possibility of formation of substitutional solid solutions between their apatites. For the preparation of these solid solutions co-precipitation from solutions containing the required ions was preferred to crystallization from fused mixtures of the end-members. A justification for such a preference is that fusion requires divergent temperatures for the apatites resulting invariably in decomposition due to inequalities in their thermal stabilities.
2.4.2 Aspects concerning precipitation of samples

It is evident that $PO_4^{3-}$ and $VO_4^{3-}$ ions which are required for the coprecipitation of solid solutions of LPA and LVA are the products of the third stage of dissociation of the corresponding orthoacids. Since the three stages of dissociation of these acids are pH-dependent, the selection of an optimum pH is important for such precipitations. It can be shown from a knowledge of the dissociation constants of these acids that a pH in the vicinity of 12 is the most optimum for this purpose. The particle size of the precipitates of apatites is usually in the range of colloidal dimensions, consequently in a pronounced surface activity. Such samples are characterised by a series of surface reactions with environmental ions of the medium of precipitation. The conditions of precipitation of LPA, LVA and their solid solutions were therefore so chosen that the environmental ions prevalent had no surface interaction with the precipitates. The temperature of precipitation of the samples was maintained at $37^\circ$C in order to simulate biological conditions since the subsequent investigations to be undertaken with the samples were intended to understand the mechanism of biological processes like calcification and resorption. The various theoretical aspects associated with the formation, properties and purity of precipitates have been incorporated in an excellent review by Salutsky.
It is well known that nucleation governs the nature and purity of the precipitates formed, the phenomenon being defined as the process of generating the initial fragments of a new and more stable phase capable of further spontaneous development. When numerous nuclei are formed the precipitation will be rapid, individual crystals small, filtration and washing difficult and purity low. Nucleation can be shown to be favoured, inter alia, by an increase in the concentration of the reacting solutions, a decrease in temperature and the presence of suspended impurities which function as seeds for its occurrence. The parameters are consequently to be appropriately controlled for the formation of precipitates of desired specifications. The rate of precipitation is another important parameter deciding the crystal size of the resulting samples. A slow precipitation, as shown, results in the formation of large well-shaped crystals minimising the occurrence of crystal defects and imperfections. This can be accomplished by the addition of a very dilute solution of the precipitant accompanied by stirring to a medium in which the precipitate is sparingly soluble. Such a condition favours, in addition, recrystallisation of the precipitate on digestion, promoting thereby further growth of the individual crystals. Based on a knowledge of the various mechanisms by which impurities may be incorporated,
a few conditions such as use of dilute solutions, slow
addition of precipitant, maintenance of a high temperature
for precipitation, digestion and washing of the precipitate
with a suitable wash liquid are considered optimum for their
minimization. The various aspects of the experimental
procedure adopted for the preparation of the samples in
order to minimize crystal imperfection and to obtain large,
well defined crystals were based on the theoretical principles
of precipitation mentioned above. To supplement the chosen
set of conditions of precipitation, the samples were sintered
at an appropriate temperature.

While the conditions of existence and methods of
preparation of tertiary phosphates and hydroxylapatites of
alkaline earths were thoroughly investigated and fairly well
established, studies on the corresponding salts of heavy
metals were found to be of limited success.\textsuperscript{98,242} The preparation
of the tertiary phosphates of heavy metals through precipitation
from aqueous media was associated with the complications due
to the coprecipitation of their hydroxides and acid phosphates.
In addition, the precipitates were found to be amorphous
and of indefinite composition. Out of the experimental
\textsuperscript{45} techniques suggested by Klement\textsuperscript{98,242}, Rathje and Hayek\textsuperscript{45},
for the preparation of the tertiary phosphates of heavy
metals, the one suggested by Hayek with appropriate
modifications was found to be suitable for the systems
investigated. It involves a complexing of the heavy metal
ions in an alkaline medium through a judicious selection of
an appropriate complexing agent. The complex was mixed with a solution of the desired anion and then made to dissociate by lowering of the pH of the medium. The tendency of lead to form well-defined soluble complexes with ethylenediamine and its monosubstituted derivatives as ligands was established by Keller and Eyke through polarographic investigations. The complexes were found to be of the type \( \text{PbL}_2 \) where \( \text{L} \), the ligand, was shown to be either ethylenediamine or its N-substituted derivative. Lead ions present in the solution, used as one of the precipitants for the preparation of solid solutions of LPA and LVA can thus be bound to ethylenediamine as a soluble complex. As the solutions used for the precipitation of apatites were to be maintained at pH 12, such a complexing could prevent the precipitation of lead hydroxide. Such a method of indirect availability of \( \text{Pb}^{2+} \) ions, functioning as precipitants, had the additional advantage of slowing down the rate of precipitation resulting in the formation of larger and more perfectly shaped crystals.

2.4.3 Theoretical Basis for characterization of the samples:

The theoretical aspects involved in the analytical procedures adopted for characterization of the samples through chemical analyses merit no special mention in this context since routine quantitative determinations were made use of. However, a striking agreement between the experimental 'g' atom ratios, \( \frac{\text{Pb}}{(\text{P}+\text{V})} \), of the samples with the stoichiometric
value justifies the suitability of the preparative as well as purification techniques adopted.

Among the techniques adopted for the characterization of the samples, X-ray diffraction happens to be the most significant since it can throw light on the homogeneity of the samples, in general, and of the solid solutions, in particular. The similarity of the patterns of LPA and LVA with those of apatites of well established \(^{243}\) composition enabled their identification to be made and showed the absence of extraneous phases within the permissible limits of their detection. While fulfilment of the desired criteria justifies the formation of solid solutions of LPA and LVA over the entire compositional range, a marginal dilation in the unit cell volume consequent upon the replacement of \( \text{P} \) by \( \text{V} \) (Covalent radii 1.10 Å and 1.22 Å respectively) is anticipated. An examination of the patterns of the samples could reveal a systematic shift in the 2θ values of the corresponding characteristic diffraction lines of apatites justifying such an anticipation and providing thereby a proof for the homogeneity of the samples. A more convincing evidence for such a dilation was provided by the excellent regularity with which the unit cell volumes of the samples, calculated on the basis of the experimentally determined lattice constants, increased with an increase in the proportion of LVA in the samples. A systematic replacement of \( \text{P} \) by \( \text{V} \) in the LPA lattice resulting in the
formation of solid solutions over the entire compositional range could thus be substantiated by the validity of Vegard's law which states that for a homogeneous series of solid solutions the unit cell volume varies linearly with composition. In addition, a striking sharpness of the diffraction lines in all the cases could suggest the crystal dimensions of the samples to be uniformly large as supplemented by the electron-microscopic investigations.

An additional confirmation of the identity of the samples could be provided by their electronmicrographs which function as a means of visual examination of the shape of the individual crystals. Earlier studies could indicate that crystals of apatites are primarily hexagonal in shape tending to hook ribbon-like, tabular or needle shaped depending upon their dimensions. The electronmicrographs of the samples of LPA, LVA and a representative solid solution could prove the existence of such a crystal shape, confirming thereby their identity as apatites. As in the case of X-ray powder patterns, the absence of extraneous phases could be confirmed through electronmicroscopy. The approximate specific surface areas of these samples were calculated by assuming the individual hexagonal crystals to be cylindrical.

The similarity of the i.r. absorption spectra of
LPA, LVA and their solid solutions could confirm convincingly the identity of these samples supplementing thereby the evidence obtained by chemical, X-ray and electronmicroscopic analyses.

As mentioned earlier the i.r. absorption peaks characteristic of $\text{PO}_4^{3-}$ (1040 and 960 cm$^{-1}$) and $\text{VO}_4^{3-}$ (800 - 735 cm$^{-1}$) function as a means of the homogeneity of the solid solutions in addition to the evidence provided for the identification of the end-members. As expected, with a progressive replacement of $\text{PO}_4^{3-}$ by $\text{VO}_4^{3-}$ the area of the i.r. absorption peak of the latter increased at the cost of the former. Absence of extraneous peaks in the pattern could eliminate the possibility of contamination of the samples. It is evident that thermogravimetric analysis of precipitated samples provides, among others, information regarding their thermal stability. Since the precipitated samples of apatites are to be heated to appropriate temperatures to drive out volatile impurities without inflicting thermal decomposition, a knowledge of their thermal stability range is essential. Keeping this objective in view, a couple of representative samples, namely, the end-members, LPA and LVA, were subjected to such studies, as mentioned earlier. While a temperature suitable for the purpose was found to be 300°C, the studies were inconclusive to throw light on the exact decomposition temperature and the nature of water associated with the samples.
2.5 Summary

Lead phosphate apatite, lead vanadate apatite and a series of their solid solutions spread over the entire compositional range were prepared by precipitation from aqueous media at 37°C by a method specially developed for the purpose. They were characterized by the conventional chemical analyses as well as by X-ray, electronmicroscopic and i.r. studies. As was to be anticipated from the covalent radii of P and V (1.10 and 1.22 Å respectively) the X-ray studies could show a systematic increase in the lattice constants consequent upon a dilation of the unit cell, with an increase in the proportion of LVA in the solid solutions in agreement with Vegard's law. The electronmicrographs of a few representative samples confirmed the absence of extraneous phases and enabled calculations of their approximate specific surface areas and the average dimensions of the individual crystals. An additional indication about the homogeneity of the samples was provided by i.r. absorption studies. As anticipated, the area under the vanadate peak increased at the cost of that under phosphate peak with a progressive increase in the proportion of $VO_4^{3-}$ in the solid solutions. Thermogravimetric studies on a couple of representative samples established 300°C as a suitable temperature for removal of volatile impurities without causing decomposition of the samples.