The history of lead usage spans some 5000 years. Lead has found considerably wider usage than its natural abundance might suggest. The role of lead in glass manufacture and in particular lead crystal is outlined. Problems involved in replacing lead in glass are discussed. While lead is one of the oldest industrial poisons, it is only in the latter part of this century that it has been elevated to the status of a premier environmental concern. The consequences of this have been acute. The roles of international bodies such as the Organisation for Economic Co-operation and Development (OECD), the World Health Organisation (WHO) and the International Program on Chemical Safety (IPCS) in reducing exposure to lead are reviewed.

1 Lead

Lead consists of four stable isotopes, $^{204}\text{Pb}$, $^{206}\text{Pb}$, $^{207}\text{Pb}$ and $^{208}\text{Pb}$. The latter three arise from decay of the radioactive series $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ respectively. Unlike gold for example, lead rarely occurs in the elemental state, rather it occurs as galena ($\text{PbS}$), carbonate ($\text{PbCO}_3$) and anglesite ($\text{PbSO}_4$). The use of lead began in the neolithic era, around 3500 BC so that the history of lead use spans some 5000 years. Lead is a most ubiquitous metal in that it has found many uses. Since it occurs in highly concentrated ores from which it is readily extracted, the availability of lead is far greater than its natural abundance might suggest. Its environmental significance derives from both its utility and availability.

The desire for silver, an important economic indicator in early times, was the principal driving force for lead production. For each ton of silver produced, approximately 400 tons of lead metal were first smelted from ores. The silver was separated from the lead by a process known as cupellation, perhaps the oldest metallurgical process. The metals were melted in a cupel or crucible at ca. 1100 °C. Air was blown onto the fused metals and this oxidised lead to litharge ($\text{PbO}$) which floated on the surface of the melt and was mechanically removed. Silver, which is much more difficult to oxidise, was not oxidised under these conditions, and could be recovered in a relatively high state of purity. Apart from its use in cupellation, the uses of lead range from the production of ornaments to the construction of the hanging gardens in Babylon some 4000 years ago. It was also used extensively in enamels in pottery glazes; a procedure now largely discontinued in many countries, and in cosmetics which whiten the face. Organolead additives were also widely used to improve the octane ratings of gasoline. The use of lead to improve the quality of glass probably originated in Egypt as evidenced by the wall paintings found at Tel-el-Emara showing the various stages of glassmaking. Lead is also widely used in lead–acid batteries, in piping, solder, cable sheathing, radiation shielding and ammunition while ‘white lead’, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ was very extensively used until relatively recently as a major component of white indoor paint.

Fig. 1 sketches lead use patterns over the past 5000 years while Fig. 2 shows the distribution of lead use by percentage category of use in 1990.¹

2 Glass²⁻¹⁰

2.1 Definition of glass

‘Glass’ is a term frequently used by most people. Few of them will however have reflected on the definition of the material or its typical properties. Glass is often described as ‘a liquid’ or ‘undercooled liquid’. A more stringent way of defining the material is the following:

‘glass is a melt that has solidified without being subject to crystallisation’.

The latter definition can be regarded as sufficient for most industrial applications. A glass can, however be produced or synthesised by routes other than melting solid substances and quenching the melt. Condensation of gaseous components or transforming liquids via a gel state to a glass are alternative ways of glass making. To exclude the production route from the

Michael J. Hynes is a lecturer in inorganic chemistry at University College Galway. He obtained his BSc and PhD degrees in Chemistry at Galway following which he carried out postdoctoral research with Ralph G. Pearson at Northwestern University in Illinois. Thus began his interest in the kinetics and mechanisms of inorganic reactions. He also spent some time with the Eigen group in Göttingen as a Senior Ciba-Geigy Fellow. His current research interests include the kinetics and mechanisms of inorganic reactions, mineral supplementation, risk assessment of chemical substances and the chemistry of lead crystal.

Bo Jonson studied inorganic chemistry at the University of Lund where he obtained both his BSc and PhD degrees. He joined Glafo in 1988 and since 1990 has been research manager there. Glafo is a non-profit membership organisation which provides R&D and technical support for Scandinavian glass producers as well as crystal producers in the UK, Ireland and France. Bo Jonson’s own research at Glafo is concentrated on subjects related to the crystal industry. These include glass chemistry, lead-free batch formulations, colour origin and improved glass quality.

Michael J. Hynes

Bo Jonson
2.2 Structural aspects of glass

The classic theory of glass structure dates from the 1930s and was formulated by Zachariasen. He described glass as a network and postulated both coordination and bonding criteria for the components in the glass (Zachariasen's Rules). In the opening sentence of his classic 1932 paper entitled 'The Atomic Arrangement in Glass' Zachariasen states, 'It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses'. While the ideas and work of Zachariasen are still valid today, modern X-ray and spectroscopic techniques in combination with kinetic and thermodynamic considerations have contributed significantly to our current knowledge of glass structure in terms of bonding distances, atom distances and coordination polyhedra. For the purpose of this review we may think of the glass structure as a continuous random network possessing medium range order rather than a disordered amorphous material.

For glass where silica is the dominant component, a model using the concept of a depolymerised silica structure can be useful. Two principal types of Si-O bonds can be found: 'bonding' i.e. those bonding to additional Si atoms and 'non-bonding' i.e. those bonding to other components of the material. Adding additional components to silica, i.e. making a silicate glass, increases the degree of silica depolymerisation and consequently the average number of non-bonding Si–O per Si. The latter number can be used for a description of the glass in terms of the expected structural units.

The understanding and theories of glass structure are however probably best developed for vitreous silica or quartz glass. An increase of the number of components complicates the description. A general model for glass structure in relation to its physical properties is lacking. This is probably due to the complexity of modelling a non-crystalline structure built from up to 15 components.

3 Chemical constitution of glass

3.1 Silicate glasses

A wide variety of substances can be transformed to or form glasses. Examples include organic compounds, elements, oxides, halogenides, chalcogenides. From a technological point
of view, the expression ‘glass’ in most cases refers to a vitreous material based on silicates and produced by use of quartz sand (SiO₂) as the dominant ingredient. Silicate glasses are described with their chemical components formulated as oxides, disregarding (or lacking knowledge of) the type of compounds actually formed in the glassy matrix. The chemical composition is usually given as mass% or mol% oxides. The development of special optical glasses has led to research and development on a variety of non-silicate glasses. The description of those, however outside the scope of this review.

The ingredients of a glass batch† may be conveniently discussed in terms of their structural and technological functions. With this in mind, the following sections will discuss the chemical composition of glass in terms of network formers, fluxes, stabilisers, refining agents and colouring/decolouring elements.

3.2 Network or glass formers
In silicate glasses, the network is comprised of silica which is probably present in the form of anionic irregular ring structures. The quantity of silica in a silicate glass is normally between 50 to 75 mass%. Lower amounts (up to 5 mass%) of the glass forming oxides B₂O₃ and P₂O₅ may also be present in a silicate glass.

3.3 Fluxes
The melting point of quartz sand is approximately 1730 °C. To facilitate the melting, or more strictly, to lower the viscosity of the melt, Si–O–Si bond breaking compounds are introduced. This is achieved using a variety of elements termed fluxes; however the most commonly used are the alkali metals. The quantity of fluxes present ranges from 10 to 20 mass%. For cost reasons, lithium, sodium and potassium carbonates are the only ingredients normally used in a glass batch.

Viscosity is a critically important factor in forming hollow lead crystal items such as stemware using either hand-blown or moulding operations, hence the need to carefully control it. In order to form a piece of hollow stemware such as a wine glass in a handblown operation, a ‘gather’ of glass is taken from the furnace on the end of a hollow steel tube called a blowing pipe. The craftsman blows through the blowing pipe to form a bubble within the gather of glass. The body of each piece is blown in a water cooled mould which determines its shape. The moulds are usually made of graphite and lined with cork. A jacket of steam causes coloration due to coordination of oxygen donor atoms to the metal ion. The resultant colours are often analogous to those found in aqueous solutions of the corresponding ion. Chromium(III) gives rise to an intense green colour and is used in the manufacture of green bottles. Iron(II1) gives rise to an intense yellow–green colour, which is shifted towards a more intense blue–green colour upon reduction to iron(II). For some transition metal ions, the chemical composition and the resulting structure of the base glass influences the colour obtained.

3.4 Stabilisers or modifiers
A two component alkali silicate glass is also known as ‘water glass’ and is water soluble. The introduction of di-, tri-, tetra- or penta-valent elements renders the glass durable towards attack by water. The introduction of additional components, i.e. modifiers, affects the chemical and physical properties of the glass. In practice, systematic variation of the modifier content is employed when reformulating the chemical composition in order to achieve the desired properties. From 10 to 35 mass% of modifiers may be present. Non-colouring modifying elements for silicate glasses may be classified in terms of the oxide groups:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Divalent</th>
<th>Trivalent</th>
<th>Tetravalent</th>
<th>Pentavalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>CaO, SrO</td>
<td>BaO, ZnO</td>
<td>TiO₂, ZrO₂, SnO₂</td>
<td>Ta₂O₅, Nb₂O₅</td>
</tr>
</tbody>
</table>

† Batch: the mix of all necessary raw materials that is charged to the melting furnace.

3.5 Refining agents
The glass batch contains compounds in which binary anions, typically carbonates, are present. Melting of the batch, at temperatures up to 1500 °C, causes decomposition and carbon dioxide evolution. Most of the gas will be transported away by the flue gases in the furnace, however some remains, together with air and batch humidity, as gaseous inclusions in the melt. The removal of the gas bubbles is called refining and operates by two mechanisms. One is pure physical bubble-rise according to Stoke’s law, the other is chemical dissolution of the remaining gas in the melt. Both mechanisms are facilitated by the addition to the batch of compounds referred to as refining agents; these result in gas evolution or sublimes. They also affect the redox chemistry of the melt. Three of the most commonly used combinations are:

- Redox active: As₂O₃ and/or Sb₂O₃ or CeO₂ in combination with an oxidising agent, most frequently sodium or potassium nitrate.
- Sulfate: sodium or calcium, often in combination with coke.
- Salts: various chlorides or fluorides, nowadays rarely used due to their adverse environmental impact.

3.6 Colouring/decolouring agents
Colour in glass can be generated by four basic mechanisms.

(a) Colouration by addition of transition metal ions
Introduction of first series transition metals into a silicate glass causes coloration due to coordination of oxygen donor atoms to the metal ion. The resultant colours are often analogous to those found in aqueous solutions of the corresponding ion. Chromium(III) gives rise to an intense green colour and is used in the manufacture of green bottles. Iron(II1) produces a rather weak yellow–green colour, which is shifted towards a more intense blue–green colour upon reduction to iron(II). For some transition metal ions, the chemical composition and the resulting structure of the base glass influences the colour obtained.

(b) Coloration by non-metallic elements
Selenium and sulfur may be utilised to colour glasses, either on their own or in combination with other elements. Sulfur can cause yellow–brown colours, selenium yellow or pink depending on the composition of the host glass. Sulfur and selenium may be used to modify the coordination environment around a transition metal colouring element in a silicate glass. They coordinate to them and thus give rise to different ligand fields. Iron–sulfur chromophores result in amber or brown glass while cadmium–selenium/sulfur chromophores produce red.

(c) Colouration by colloidal particles
The coinage metals, copper, silver and gold can be dissolved in a silicate glass and heat treated under rather strict conditions to form colloidal metallic (probably oxides in the case of copper) particles of nanometre size. These give rise to yellows or reds.

(d) Decolouring
In common with all industrial processes, glass manufacturing is influenced by process costs. The raw materials used for most glass making are not reagent grade chemicals as used in laboratories, but rather minerals or bulk chemicals. As a result green/yellow colouring contaminants such as Fe₂O₃ and Cr₂O₃ will be introduced into the glass. When producing a clear colourless glass, the colours produced by the contaminants are compensated for by addition of small amounts of elements which generate the complementary colours, thus giving a grey or slight pink/violet/blue tint to the glass.
4 Examples of typical lead-containing silicate glasses

4.1 Optical glass
Optical glasses, designed to cover a wide and strictly defined range of refractive indexes and dispersions, were traditionally composed of silicate glasses. Lead was introduced to increase refractive index and dispersion (variation in refractive index with wavelength). Optical glasses may have a lead content which can vary from just a few mass% to more than 50 mass% PbO. Table 1 shows the composition of optical glass F8 having a refractive index \( n_D \) of 1.5955 and dispersion \( \nu \) of 39.18.

4.2 Sealing glass
Sealing glasses are used to join metals to glass in a variety of products. The demands for matching thermal expansion and good adhesion are high. The insulating properties of glasses are advantageous when used in electronics. Lead is also used in some of these glasses. A typical composition is shown in Table 1.

4.3 Cathode ray tube glass
The cathode ray tubes used in televisions and monitors utilise three different types of glass in the screen, cone and neck respectively. While lead has been used in all of the glasses, the practice nowadays appears to be that only the neck which contains the glass–metal joint is made from a lead-containing glass. A typical composition for a cathode ray neck tube glass is shown in Table 1.

4.4 Crystal
Crystal or lead crystal is the term used to describe a glass composition used for hand or machine based production of more decorated glass items. According to an EU directive\(^{11}\) a glass traded within the EU must contain more than 24% PbO to be called ‘crystal’. The directive also states minimum values of refractive index \( n_D \) (1.545) and density (2.9 g cm\(^{-3}\)). These minima are however the minimum values expected from a glass having such a lead content. Lead gives the glass properties favourable for this type of production, as will be discussed later. Typical compositions are shown in Table 1.

5 Physical and chemical properties of melts and glasses—special emphasis on the impact of lead

5.1 The relation between composition and properties
An alteration in the ratio of the components in a silicate glass will result in changes in the physical and chemical properties. These are however, the sum of the influences of all components on the glass structure, so that not only one, but many properties will be affected upon altering the chemical composition. This is schematically described in Fig. 4. Fig. 4 implies that for instance increasing the amount of Na\(_2\)O in order to reduce the viscosity also results in increased thermal expansion (\( \alpha \)) and reduced durability. Because of the effect on many properties of one component, all glass compositions used in manufacturing can be regarded as compromises, with some critical properties at optimum and the remainder at acceptable levels.

As previously stated, there is no available structural model for predicting the relationship between composition, structure and properties. The methodology applied for calculating the relationships between properties and composition is based on experimental data. Data on known glass compositions and measured properties over a well-defined range of compositions are treated by mathematical/statistical means. From the analysis, a model is designed to describe and calculate the relationships between the chemical composition and properties of interest.

5.2 Viscosity
The viscous flow–temperature dependence of the melt is probably the most crucial technological parameter in glass production. It determines the thermal input requirements, furnace design and materials and sets requirements for forming equipment and conditions. The viscosity of a glass (\( \eta \)) ranges over several orders of magnitude during the melting process. Viscosity is frequently described by the so-called Vogel–Fulcher–Tamman (VFT) eqn. (1).

\[
\log \eta = \frac{A}{T - T_0} + \frac{B}{T}
\]

where \( \eta \) is viscosity (dPa); \( T \) is temperature and \( A, B, T_0 \) are constants.

The viscosities of some silicate glasses are plotted using the VFT equation in Fig. 5. It is apparent that the lead glass has a smooth curve; this results in a long temperature range (or time) for the forming process. Such glasses are termed ‘soft’ or ‘long’

**Table 1. Chemical composition of glasses**

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>Optical glass F8 ((n_D: 1.5955, \nu: 39,18))</th>
<th>Sealing Glass</th>
<th>Cathode ray tube ((&gt; 30% \text{ PbO}))</th>
<th>Lead crystal ((&gt; 24% \text{ PbO}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}_2 )</td>
<td>50.2</td>
<td>57.1</td>
<td>56.2</td>
<td>55.2</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>—</td>
<td>1.5</td>
<td>1.7</td>
<td>—</td>
</tr>
<tr>
<td>( \text{B}_2\text{O}_3 )</td>
<td>0.4</td>
<td>—</td>
<td>—</td>
<td>0.6</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>3.8</td>
<td>4.9</td>
<td>4.2</td>
<td>0.4</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>5.6</td>
<td>7.0</td>
<td>8.4</td>
<td>11.7</td>
</tr>
<tr>
<td>( \text{PbO} )</td>
<td>39.7</td>
<td>29.5</td>
<td>29.3</td>
<td>31.8</td>
</tr>
<tr>
<td>( \text{ZnO} )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
</tr>
<tr>
<td>( \text{As}_2\text{O}_3 )</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
</tr>
<tr>
<td>( \text{Sb}_2\text{O}_3 )</td>
<td>—</td>
<td>—</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

136 Chemical Society Reviews, 1997
glasses. Another characteristic of the lead glass is a low transformation region; thus lead glasses are suitable for low temperature glazing purposes.

5.3 Crystallisation
Extensive crystallisation or devitrification of all glasses can be induced by thermal treatment. The kinetics and phases separated are largely influenced by the chemical composition and presence of nucleating agents. Lead-containing glasses are found to be stable towards crystallisation and they exhibit low liquidus temperatures. Crystallisation is often found to be initiated at the surface. This is likely due to lead evaporation from the surface resulting in a change in the chemical composition tending towards alkali silicates which have different crystallisation characteristics.

5.4 Surface tension
Although surface tension is also a parameter of prime importance in glass technology, its impact on processes related to glass production is not fully understood. Surface tension is largely dependent on the overall chemical composition of the melt. The Na₂O/K₂O ratio has a significant influence on the surface tension. The introduction of large quantities of lead results in a large decrease in surface tension. For example, at 1300 °C the surface tension for a lead-containing glass can be expected to be ca. 200–230 mN m⁻¹ or 20% lower than in lead free silicate glasses having similar viscosities and applications.

5.5 Thermal properties
Specific heat and thermal conductivity, properties most relevant at higher temperatures, are less sensitive to variation in either temperature or chemical composition. Lead has little influence on these parameters, however high-lead glasses have been reported to have thermal conductivities at the lower end of the narrow range of variation. Thermal expansion is to a large extent influenced by the overall chemical composition. Most components, apart from SiO₂ and B₂O₃ cause an increase in the thermal expansion coefficient. The effect of lead is rather

![Viscosity-temperature curves for silicate glasses. A: soda lime glass, B: lead crystal glass, C: unleaded crystal.](image-url)
modest, with alkalis having the most pronounced effect on this property.

5.6 Electrical properties
The electrical properties of a glass melt (solid glass is insulating) are of technical interest when using electrically heated furnaces. Conductivity in a glass melt arises from the mobility of fluxing and stabilising ions. Alkali metal ions cause the greatest increase in conductivity while lead causes a reduction.

5.7 Mechanical properties
The factors influencing the mechanical properties of glass are difficult to quantify. For instance, the tensile strength is not only dependent on the chemical composition, but also on sample size and surface conditions of the test specimen, test procedure, thermal history etc. Nevertheless, some properties of interest can be briefly discussed.

The modulus of elasticity is strongly dependent on the chemical composition. Lead reduces the value of this property significantly to ca. 60 GPa; this is some 15-20% lower than for lead-free glasses. Surface hardness is also dependent on composition. Lead has a similar effect on hardness as on the modulus of elasticity in that the hardness is significantly reduced on introduction of lead. This greatly facilitates mechanical treatments such as cutting, grinding and polishing. However, the softer lead glasses will also be more readily scratched by uncontrolled mechanical forces.

5.8 Optical properties
The optical properties most frequently discussed in relation to glass are the refractive index \(n\) for any wavelength, and dispersion \(n-F\) and reciprocal dispersive power. The dispersive property is commonly expressed as the Abbe number \(v\) [eqn. (2)] where \(C\) (red hydrogen line 656.3 nm), \(D\) (yellow sodium line 589.3 nm) and \(F\) (blue hydrogen line 486.1 nm) represent the relevant Fraunhofer lines of the spectrum of the Sun.

\[
v = \frac{1}{(n_c - 1)/(n_F - n_c)}
\]

A typical lead crystal containing 24% PbO will have an Abbe number of ca. 48. Both refractive index and dispersion are strongly dependent on the chemical composition and are affected by alterations to it. The influence of a modifying element on those properties does not necessarily have the same effect, i.e. a substitute increasing the refractive index may not necessarily increase the dispersion (decrease in the Abbe number). TiO\(_2\) is probably the oxide contributing most to an increase in both refractive index and dispersion in silicate glasses. The effect of PbO is similar to that of TiO\(_2\).

5.9 Colouring properties
The origin of colour in silicate glasses has been briefly discussed above. No primary effect on colour is expected from the introduction of lead in a silicate glass, although yellowish colouration has been reported for high lead glasses. The latter effect is probably due to contaminants originating in either the raw materials or the crucible. Lead glasses show strong absorption in the ultraviolet spectral region. This can result in secondary effects on the colour originating from ionic or elemental colour centres as discussed above. Another secondary effect can be ascribed to the structure of lead glasses and the fact that several lead glasses contain little or no sodium or lithium but rather potassium as fluxing component. For instance, NiO colours lead-potassium glasses purple but results in a brownish colour in lead-sodium host glasses. Selenium colours lead glasses yellow, but gives rise to a pink colour in non-lead glasses.

5.10 Density
Density is also an additive property of the glass components. Lead is one of dominant components in increasing the density. 30% PbO glasses have densities of ca. 3 g cm\(^{-3}\). Increasing the lead content to 60% might double this value.

5.11 Chemical durability
The durability of glasses is a very complex subject. A variety of standardised test methods have been described covering a wide range of media and ambient conditions, the thermal history, storage conditions and treatments of the glass item also influencing the result. In general, the higher the silica content in a silicate glass, the more stable towards attack it is. Addition of alkali metals results in a significant deterioration in durability. With regard to the effects of modifying elements, it is difficult to find one single general pattern. One investigation reports increased durability when substituting Na\(_2\)O in the system Na\(_2\)O-SiO\(_2\) with equimolar amounts of CaO, MgO, PbO and ZnO. In this case, ZnO resulted in the greatest improvement in durability, however, this may not necessarily be so for other glass compositions or indeed for other test methods.

6 Advantages and disadvantages of lead in glass
In a summary of the above section on the properties of glasses relevant to technology and manufacturing, several benefits of lead can be identified. Lead makes the glass soft, both in the melt and as a solid glass being processed. It gives the glass high values of desirable physical properties such as density and refractive index, properties used for classification of crystal glasses. It promotes a low deformation temperature, useful for low temperature glazing procedures.

Some technological drawbacks can also be identified. The soft glass is easily damaged during handling thus increasing the number of repairs necessary. The long viscosity may result in lower productivity at the hot end working process. Lead is volatile and both the work place and the environment are exposed to lead oxide vapours during manufacture of lead glasses.

The most serious drawback of lead is of course its well documented adverse impact on the environment and health. This may eventually lead to its eventual replacement as is occurring in gasoline.

7 Substitution of lead in silicate glasses
It is difficult to find one single element which promotes in an alkali silicate glass all the properties achieved by the introduction of lead. It imparts high refractive index and high dispersion without colouring the glass. It provides economic melting temperatures and a long working temperature range suitable for the traditional hand-working methods, high density, a hardness suitable for mechanical cutting together with a chemistry suitable for acid polishing following the cutting process. Finally, all these properties are provided at an economic cost. From a chemical and structural point of view, the neighbouring element bismuth, present in the glass as Bi\(_2\)O\(_3\), gives similar properties to lead. However, due to cost and availability, bismuth is a less than ideal substitute. The total quantity of bismuth currently mined would only substitute approximately 10% of the lead currently used by the crystal industry. The cost of the raw material is some ten times higher than lead oxide, resulting in unrealistic process costs.

From the point of view of the crystal industry, two principal ways of substituting lead in crystal can be identified. One is the use of rather high amounts of BaO together with minor additions of other modifiers. This results in glasses having high densities and refractive indices and melts having viscosities suitable for hand-working. However, the widespread use of barium as a lead substitute has been questioned, primarily due to

\[\ddagger\] Hot end: this refers to procedures applied when the glass is in the melt stage, i.e. at temperatures higher than the transformation range. Forming the melt to the desired shape is the dominant activity.
the toxicity of soluble barium compounds. The other route

towards unleaded formulations has been the use of combina-
tions of the modifiers mentioned above. For cost reasons,
a suitable combination of CaO, MgO, SrO and ZnO together with
smaller additions of other modifiers, results in glasses having
properties similar to those of lead crystal.

In general, the unleaded formulations will be expected to
show a somewhat shorter hot-end working range, however, this
might even be beneficial for productivity. The major changes
will be required at the cold end by working, e.g. cutting, grinding
and polishing. The cold-end processes currently in use have
been developed over many decades and have been optimised for
soft lead glasses having well known chemical and physical
surface properties. The use of harder glasses having different
surface properties will dramatically change the requirements for
these processes.

8 Lead as an environmental issue

Lead is one of the oldest industrial poisons. Contamination by
industrial lead has occurred everywhere on the earth. Estimated
natural emissions of lead aerosols to the Earth’s atmosphere are
estimated to be only 1/100 those of industrial lead emissions.12
This point is amplified by the knowledge that the skeletal lead
concentrations in typical Americans in 1980 were elevated some
500-fold above the natural concentrations measured in the
bones of Peruvians who lived in a relatively unpolluted
environment some 1800 years ago.

The Agency for Toxic Substances and Disease Registry
(ATSDR) ranks lead as its prime concern13 while the EU’s
concern regarding lead toxicity is highlighted by the fact that it
is one of the few elements for which not only are specific
regulations in place to protect workers from exposure to it.14
There is also a Directive on biological screening of the
population for lead.15 Lead is now one of the premier
environmental concerns and pervasive lead poisoning is the
principal environmental health issue for American children.
How did this come about? Why is lead such an issue compared
to other toxic elements such as arsenic, cadmium and mercury?

Table 2 Criteria for ranking lead exposure/lead poisoning as an environ-
mental health issue

| Table 2 | Criteria for ranking lead exposure/lead poisoning as an environ-
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| 1 Economic and sociopolitical | (a) Economic and historic centrality
(b) Dominance of economic/social over health issues
(c) Limited scope of decision making
(d) Control of research and information
| 2 Scientific and public health | (a) Indestructible—accumulates in environment and body, multimedia contaminant
(b) Toxicity in numerous organisms/systems with few protective barries
(c) Toxicity with low or no threshold in huge numbers of the most vulnerable
(d) Effects persist in target organs
| 3 Societal risk assessment | (a) Adverse health effects across total spectrum of detection, preclinical and clinical
(b) Compelling evidence of widespread toxicity is present
(c) Requires role for both environmental control/preventive medicine and traditional medical interventions
(d) Requires use of societal-level (macro risk) and individual (micro level) components of cost-benefit analyses

The high rank of lead as an environmental contaminant is readily visualised when the position of lead as a global

$\text{Cold end: this refers to procedures applied to a cooled glass, commonly at room temperature.}$

§

Economic commodity is examined. Since the introduction of
cupellation, the total world production of lead is estimated by
Flegal and Smith16 to be ca. 300 million metric tons. Total
world consumption up to 1989 is estimated to be 275 million
tons. Mercury also has a long history in that its earliest use
occurred some 3500 years ago17 and by the first century AD, the
Roman population was consuming 4.5 metric tons per annum.
Total production of mercury since it was first used is estimated at
78000 metric tons. Cadmium is a relative newcomer to the
industrial scene and while significant quantities were produced
during the production of zinc, most of it was discarded and it is
only in ca. 1910 that commercial production began. Total world
production to date is estimated at ca. 1.4 million metric tons.
Arsenic is produced as a by-product during copper production and
its commercial production dates to the beginning of the
nineteenth century, a total production span of ca. 190 years.
Total world production is estimated at ca. 78 million metric
tons.

From the foregoing, the premier role of lead as a potential
environmental contaminant can be readily appreciated. It has
been used for longer than the other elements and significantly
larger quantities of it have been produced and used.

9 History of lead toxicology

Castellino19 provides a detailed history of the incidence and
recognition of the adverse effects of lead. The first documented
case of an illness which can be definitely ascribed to lead
poisoning is ascribed to Hippocrates (fifth to sixth century BC) who
described a severe colic in a worker involved in extracting the
metal. Marcus Vitruvius Pollio (first century BC) who lived in
the time of Caesar and Augustus noted the sickly appearance
of people who were in contact with lead and Pliny also noted
similar effects. Lead was widely used by the Romans in
plumbing, with tin as an alloy for making kitchen utensils, as a
sweetener in cooking, a food additive and for the preparation of
alcoholic drinks. The main source of lead poisoning for the
Roman aristocracy was 'grape syrup'. This was made from
unfermented grape syrup and was boiled down to a third of its
original volume in lead-lined bronze cauldrons.

Despite these early reports of the adverse effects of lead, the
public health history of lead is surprisingly short and is virtually
non-existent for some 98% of the time in which lead has been
used. Of the 300 million tons of lead produced, approximately
50% is estimated to have been dispersed to the various
environmental compartments.20 It is really only since the 1970s
that the pre-eminent role of lead as an environmental toxicant
has been recognised. There are many reasons for this. However,
the three main reasons are (1), (2), (3) and (4) as outlined in Table
2. The dominance of socioeconomic issues over health issues is
nothing new and many examples exist. Decision-making
regarding the use of lead as well as the control of research and
information which might highlight the adverse effects of lead
exposure was largely vested in the producers and users of
lead.

One of the pioneers in the fight against lead exposure was
Alice Hamilton. Her biography21 and the review by Lippmann22
provide a detailed insight into the difficulties she encountered in
her fight against lead. She carried out a systematic study of lead
poisoning among industrial workers in Illinois in 1910 and the
results encouraged her to embark on a career in occupational
medicine.

Tetraethyl lead has occupied a pre-eminent position as a
source of environmental lead. This is largely due to its volatile
nature and its widespread and rapid dissemination. The history of
leaded gasoline began in Ohio in 1923 when gasoline
containing lead additives was first used and since then the motor
car has played a central role in the dissemination of lead. Since
organic lead compounds were first added to gasoline in 1923,
background lead levels have increased world-wide, including
the Greenland ice cap. Hamilton first expressed her anxiety

Chemical Society Reviews, 1997 139
about the use of tetraethyl lead as early as 1925 and it is now patently obvious that failure to take account of her warnings have had tragic consequences from the point of view of public health. On May 20, 1925 the US Surgeon General convened a conference to assess the tetraethyl lead situation. The industry situation was summarised as follows: (a) leaded gasoline was essential to the industrial progress of America; (b) any innovation entails certain risks; (c) the major reason that deaths and illnesses occurred at plants was that the men who worked there were careless and did not follow instructions. Dr Yandell Henderson, a physiologist at Yale University presented severe criticism of the use of tetraethyl lead at that meeting.23 He spoke about the probability that leaded gasoline would be in universal use in cars. Arising from the conference, a special committee was established to conduct an investigation of leaded gasoline. The committee concluded some seven months later that ‘in its opinion there are at present no good grounds for prohibiting the use of ethyl gasoline . . . provided that its distribution and use are controlled by proper regulations.’ The committee saw its report as an interim one and recognising its limitations, they concluded that further studies by the Government were essential. In view of what has come to pass it is unfortunate that these investigations did not take place for more than four decades.

The tetraalkyl lead compounds added to gasoline function by decomposing at engine temperatures into atomic lead and alkyl free radicals. These atoms of lead must be removed from the engine, otherwise build-up of lead deposits would eventually destroy the engine. In order to achieve this, small quantities of ethylene dibromide and dichloride are also added so that lead is emitted as PbCl₂, PbBr₂ and PbBrCl. These are eventually converted to PbO. The lead oxide exists as particulate matter in the atmosphere for a considerable period so that it is widely dispersed. Arising from this process, a significant percentage of ingested lead has its origin in leaded gasoline. Ca. 1% of the organolead content of petrol is emitted into the atmosphere via the exhaust unchanged and the elegant studies of Harrison and his coworkers on aerosols provide details of the sources, speciation and transport modes of alkyllead compounds in the environment.

The requirement to equip cars sold in the US and Europe with catalytic converters has accelerated the conversion to the use of unleaded gasoline. This has had a dramatic effect on both ambient lead levels in air and blood lead levels in these countries as is illustrated in Figs. 6 and 7. Although only a small percentage of world lead production ends up in gasoline (Fig. 2), it represents a very efficient method of distributing lead in the environment. Leaded petrol is however still used in many countries.

10 Distribution of lead in the environment

Fig. 8 outlines the most significant contributors to current body burdens of lead.25-26 It is apparent that human intake can occur by a variety of pathways. These include inhalation of airborne particles, water, food, wines and other alcoholic drinks. It may also be ingested as a result of leaching of lead from cooking and drinking utensils.

Drinking water represents a significant source of lead for many people and in recognition of this, many Governments impose maximum concentrations of lead in drinking water. The current World Health Organization recommendation and EU limit is 50 µg l⁻¹. The concentration of lead in drinking water depends on the lead content of the water source which in turn depends on physicochemical properties such as pH and hardness. It also depends on the nature of the plumbing. Lead in food can arise from the inherent concentrations of lead present, but in certain circumstances, significant increases can arise from the containers in which the food is stored. In general, meat and other animal products make a relatively small contribution to total human lead intake due to fact that lead is not preferentially deposited in edible portions of animals. The lead content of vegetables is highly variable and depends greatly on the lead content of the soil.

In the past, canned foods contributed significantly to lead intake.22 This was due to the lead solder used in manufacturing the cans. Acidic foods and foods stored in acid media (vinegar) enhanced lead leaching/migration and significantly increased the lead content of the food. In New Zealand for example, canned food makes up 8.38% of the diet but is responsible for 34.4% of the lead intake.22 Replacement of soldered cans by welded cans is eliminating this problem.

Significant quantities of lead may be ingested by workers in industries using large quantities of lead-containing materials. This is evidenced by the relatively high blood lead levels (PbB) found in workers in these industries. In recognition of this, international organisations such as OSHA have recommended a permissible exposure limit of 50 µg m⁻³ in the working place air. The current EU limit for lead in ambient air is 2 µg m⁻³ and the WHO assume that each 1 µg m⁻³ of lead in ambient air contributes ca. 1.9 µg dl⁻¹ to a child’s blood and ca. 1.6 µg dl⁻¹ to an adult’s. A current WHO draft guideline recommend a fourfold reduction in the ambient air concentration to 0.5 µg m⁻³.

140 Chemical Society Reviews, 1997
Why is there such a concern about lead? The main reason is that the safety margin between unavoidable ingestion from food and water and levels which constitute a significant risk to health is relatively small. In the case of chemicals for which occupational exposure levels exist, these levels frequently represent safety margins of 10–1000 depending on the quantity and quality of the toxicity data available. In the case of lead, such margins do not exist. The FAO/WHO Provisional Tolerable Weekly Intake of dietary lead is 3 mg for an adult. The average person in Great Britain is estimated to have a
dietary intake of up to 0.42 mg per week, excluding the
contribution from drinking water. This same report shows that
the intake from drinking water can vary greatly from 2.5 mg per
week in areas such as Glasgow and Ayr, areas with a
plumbosolvent water supply and much lead piping to 0.19 mg
per week in Birmingham, an area where lead levels in water are
not unduly elevated.

11 Fate of ingested lead

Once ingested, lead is absorbed from the gastrointestinal tract or
excreted. The fraction absorbed varies with the nutritional state
of the victim but it is generally accepted that adults absorb on
average 10–15% of the quantity ingested while children can
absorb up to 50%. Absorption is greatly enhanced by fasting and
both iron, zinc and calcium deficiency. Typically, men in the
60–70 age bracket will have accumulated ca. 200 mg of a lead
body burden while women will have somewhat lower body
burdens. This represents an accumulation of an average of some
9 μg per day.

The ionic radius of Pb²⁺ (132 pm) is similar to that of Ca²⁺
(106 pm) and Sr²⁺ (127 pm) and in the body it has a very similar
chemistry. Once in the blood, lead is distributed primarily
amongst the compartments (a) blood, (b) soft tissues e.g.
kidney, bone marrow, liver and brain and (c) mineralising tissue
e.g. bones and teeth. Since alkaline earth elements are
concentrated by bone surfaces and mineralising tissues, it is not
surprising that they contain ca. 95% of the total body burden
of lead in adults. Lead substitutes for calcium in bone and is
incorporated into the hydroxyapatite crystal, Ca₁₀(PO₄)₆(OH)₂.
This occurs both during bone formation and remodelling arising
from bone turnover. Most of the lead ingested is excreted in the
urine with smaller quantities lost in faeces, sweat, hair and nails.
Due to bone turnover in the body, the original surface deposits
of lead are redistributed. 99% of lead in the blood is associated
with erythrocytes while the remaining 1% is in the plasma
where it is available for transport to the tissues.

The lead in mineralising tissues is distributed between two
compartments, a labile pool which readily exchanges lead with
blood, and an inert pool which poses a special risk in that it may
be mobilised in times of stress, thus providing a significant
endogenous source of lead which can significantly increase the
level of lead in the blood. In adults, it is estimated that the half
life of lead in blood is ca. 25 d, in soft tissue ca. 40 d and in the
inert pool in the bone, ca. 25 y. This highlights the risks
associated with chronic lead exposure and underlines the
difficulties of dealing with lead poisoning.

12 Health effects of lead—saturnism

A wide variety of adverse health effects arise from exposure to
lead. In earlier times lead was associated with the planet Saturn,
hence the expression ‘saturnismus’ is frequently applied to lead
poisoning. Castellino expands on several theories regarding
the origin of this analogy. Since lead is the oldest metal, it was
associated with Saturn, who was considered one of the oldest
gods on Mount Olympus. Others ascribe the association to the
fact that lead absorbs other metals and has thus been represented
by a greengrocer and the god Saturn who sold lead to children!
A graphic account of the onset of saturnism is provided in an
article by Prendergast and he reported a 9.4% fatality rate in
adults with a 6.4% fatality rate in females. Acute exposure to
lead leads to (a) gastrointestinal cholic and (b) encephalopathy
in children. However, acute exposure to lead is thankfully now
a rarity and chronic effects are more common.

Lead primarily affects the peripheral and central nervous
systems, the blood cells and metabolism of vitamin D and
calcium. There are many chronic effects arising from lead
exposure, however the following are some of the more common:

- Anaemia arising from inhibition of haem synthesis, chronic
encephalopathy, cognitive impairment, sleeplessness,
  headaches, aggressive behaviour, convulsions, disruption
  of the motor system and renal effects.

Fig. 9 shows the lowest observable effect levels (LOAEL) of inorganic lead in both children and adults.

13 Neurologic effects of lead-effects on cognitive
development in children

By far the most sensitive target of lead poisoning is the central
nervous system. In children, neurologic deficits have been
documented at exposure levels once thought to be safe. Indeed,
as recently as 1969, a blood lead level of 60 μg dl⁻¹ was thought
to be safe. In 1970, the US Surgeon General reduced the toxicity
level to 40 μg dl⁻¹. In response to research which suggested that
cognitive deficiency resulted from exposure at this level, the
Centers for Disease Control reduced the intervention level to
30 μg dl⁻¹ in 1978, to 25 μg dl⁻¹ in 1985 and finally to
10 μg dl⁻¹ in 1991.

Lead toxicity in children is a very emotive issue. The
landmark paper in this area was by Herbert Needleman and
published in the New England Journal of Medicine of 29th
March 1979. He concluded that children having high dentine
lead levels scored significantly less well on the Wechsler
Intelligence Scale for Children than children having low dentine
lead levels. This is perhaps one of the most controversial
scientific papers ever published and was subjected to much
criticism, in particular by Claire Ernhart, a psychologist at Case
Western Reserve University. Such was the controversy that the
EPA convened a special panel to examine both Needleman’s
and Ernhart’s work. They found several deficiencies in
Needleman’s work. Ironically, they also found fault with
Ernhart’s work. The controversy still rages.

Taking all the data published, it can be safely concluded that
measurable effects on cognitive development are evident in
children having blood lead levels >10 μg dl⁻¹. Postnatal as
opposed to prenatal exposure would appear to have a greater
influence on cognitive development. Nutritional deficiencies of
essential metals can increase the effects of lead exposure by
enhancing the absorption and toxicity of dietary lead. The
metals having the greatest influence are calcium, iron and
zinc.

14 Monitoring of lead exposure

Two aspects of lead are of interest. In the first the actual lead
concentrations are measured in order to provide a measure of
the dose index. The dose index most frequently used is the blood
lead concentration (PbB). This is usually expressed in terms
of μg dl⁻¹ or μmol l⁻¹ (1 μmol l⁻¹ = 20.7 μg dl⁻¹). The former
is the index used by most health authorities in setting the
maximum allowable body burden of lead and it is the index
most frequently quoted in studies of lead exposure. The PbB
represents the equilibrium existing between lead intake, reten-
tion, body stores and excretion rate. However, other indices can
also be used and it is often asserted that lead concentration in
teeth and bone provide a better indication of the body lead
burden. Urinary excretion of lead following administration
of EDTA is also used.

Considerable interest has been expressed in indices of the
biochemical effects of lead absorption. Ideally, these should
highlight effects arising from relatively low levels of exposure
before the usual clinical symptoms are manifested. Perhaps the
most widely studied biological indicator of lead exposure has
been the measurement of erythrocyte zinc protoporphyrin
(ZPP). Lead interferes with the synthesis of haemoglobin by
interfering with several steps in the haem pathway. The
incorporation of Fe²⁺ into the molecule of protoporphyrin IX
represents the final step of haem synthesis. The enzyme
ferrochelatase which catalyses the insertion of iron into

Chemical Society Reviews, 1997
### Lead concentration in blood (μg Pb dl⁻¹)

<table>
<thead>
<tr>
<th>Children</th>
<th>Adults</th>
</tr>
</thead>
<tbody>
<tr>
<td>Death →</td>
<td>150</td>
</tr>
<tr>
<td>Encephalopathy →</td>
<td>100</td>
</tr>
<tr>
<td>Nephropathy →</td>
<td></td>
</tr>
<tr>
<td>Colic →</td>
<td>50</td>
</tr>
<tr>
<td>Hemoglobin synthesis</td>
<td>40</td>
</tr>
<tr>
<td>Vitamin D metabolism ↑</td>
<td>30</td>
</tr>
<tr>
<td>Nerve conduction velocity ↓</td>
<td>20</td>
</tr>
<tr>
<td>Erythrocyte protoporphyrin ↑</td>
<td></td>
</tr>
<tr>
<td>Vitamin D metabolism ↓</td>
<td></td>
</tr>
<tr>
<td>Developmental toxicity</td>
<td>10</td>
</tr>
<tr>
<td>IQ ↓</td>
<td></td>
</tr>
<tr>
<td>Hearing ↓</td>
<td></td>
</tr>
<tr>
<td>Growth ↓</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 9** Effects of inorganic lead in children and adults—lowest observable adverse effect levels (ATSDR—toxicological profile of lead, 1989). ↑, increase; ↓, decrease.

Protoporphyrin IX is very sensitive to lead. Exposure to lead inhibits the enzyme activity of ferrochelatase and thus reduces the availability of Fe²⁺. When Fe²⁺ is not available, the enzyme binds Zn²⁺ instead and thus the concentration of ZPP in blood is elevated. It has been demonstrated that measurement of ZPP is not sufficiently sensitive at low levels of lead poisoning to be acceptable as a reliable indicator of lead exposure. However, the ZPP level in blood declines more slowly than blood lead so that ZPP levels can be an indicator of intoxication arising from lead resorbed from bone.

### 15 Chelation therapy

Chelation therapy is a therapeutic procedure in which a chelating agent is administered to a patient in order to selectively remove a toxic metal ion such as lead. Such chelating agents can act in two ways. They can increase excretion of the metal, thus reducing the body burden or alternatively they may limit absorption of the metal from the gastrointestinal tract. Ideally, the chelating agent should have a high affinity for the metal ion to be removed and have a low affinity for essential metal ions such as Zn²⁺, Ca²⁺ and Fe²⁺.

Several chelating agents have been used in the treatment of lead poisoning. Examples include calcium disodium ethylenediaminetetraacetate, 2,3-dimercaptopropanol (British Anti Lewisite, BAL), 3-mercaptopropanoic acid, 2,3-dimercaptopropanol (British Anti Lewisite, BAL), and 3-mercaptopropanoic acid, 2,3-dimercaptopropanol (British Anti Lewisite, BAL). Although CaNa₂EDTA has been used for over fifty years, relatively little is known regarding its efficacy. Succimer was the first orally administered drug to be approved by the FDA for treatment of children with blood lead levels of > 45 μg dl⁻¹. Clinical experience with all of these drugs is relatively limited and emphasis should be placed on removing the victim from the source of lead rather than on chelation therapy.

### 16 Migration (leaching) of lead from lead crystal

#### 16.1 Background

In January 1991 Graziano and Blum published a paper in which they demonstrated that significant concentrations of lead leached or migrated from crystal decanters and glasses containing port. Despite the fact that earlier papers reported similar findings, the Graziano and Blum paper achieved wide publicity and articles appeared in newspapers and magazines worldwide questioning the safety of lead crystal stemware. This caused significant anxiety in the lead crystal industry. In response, the International Crystal Federation (ICF), an umbrella organisation of European and US crystal manufacturers which was set up in April 1991, undertook an urgent investigation of the problem. International Standards ISO 7086/1 and 7086/2 regulate the release of lead and cadmium from glassware and ceramicware in contact with food. The test consists of filling the container with 4% (v/v) acetic acid and leaving it to standing at 22 °C for 24 h. The maximum...
permits the release of lead from small hollow-ware (< 600 ml) is 5 mg l\(^{-1}\) and from large hollow-ware (> 600 ml) 2.5 mg l\(^{-1}\). The ICF have adopted voluntary standards for lead migration which are significantly lower than those demanded by the ISO standard. These are 1.5 mg l\(^{-1}\) for small hollow-ware and 0.75 mg l\(^{-1}\) for large hollow-ware. In addition, they recommend that spirits should not be stored in decanters for extended periods unless the decanters have been treated to eliminate lead migration. Adherence to these guidelines will not result in any undue exposure to lead having its origin in lead crystal. Wines themselves may contain lead concentrations in the range 10–500 g l\(^{-1}\). Typical 24% PbO crystal currently manufactured is expected to leach ca. 10 μg Pb during three 1 h contacts of 150 ml of wine per contact (a total of 450 ml). Most of the leaching occurs during the first two contacts so that successivecontacts will not significantly increase the lead intake. These conditions represent an extreme case in view of the quantity ingested and the contact time. However, such an intake does not present any undue risk to the average adult, particularly in view of the fact that lead absorption during meals is less than 10%.

The leaching of lead from lead crystal glass is a diffusion controlled ion exchange process and follows Fick’s law. This is demonstrated by eqn. (3), where \( t \) is the time. The slope of the plot, \( a \), is largely controlled by the composition of the glass.

\[
[\text{Pb}] = a \sqrt{t} + b \quad (3)
\]

The ordinate value, \( b \), represents the initial “spike” released and is influenced by acid polishing\(^\dagger\) and surface treatments.

### 16.2 Reduction of lead migration

Various approaches have been used to reduce or eliminate lead leaching. These include:

- (a) The use of non-lead glass liners in decanters.
- (b) Alterations to the lead glass composition. These include slight increases in the silica content, reduction of the alkali oxide (K\(_2\)O, Na\(_2\)O) content, optimising the Na\(_2\)O/K\(_2\)O ratio and addition of trace quantities of other oxides such as MgO, ZnO.
- (c) Use of various surface treatments. These include acid polishing, ammonium sulfate fuming and the use of coatings such as sol–gels and various polymers.

**Acid polishing**

Acid polishing of lead crystal items in sulfatic acid hydrofluoric acid baths has been shown to significantly reduce lead migration by reducing the concentration of lead in the surface layer of the glass.

The use of ammonium sulfate fuming, a process pioneered many years ago by Waterford Crystal, is a remarkably simple procedure that significantly reduces lead migration. A small quantity of ammonium sulfate (0.1–0.2 g) is placed in the glassware before it is placed in the lehr for annealing. Best results are obtained when the temperature is in the range 470–490 °C. The procedure is particularly suitable for decanters, however they must be sealed before being acid polished as acid contact diminishes the impact of the ammonium sulfate treatment. The chemistry involved is believed to be as follows:

\[
\begin{align*}
100–360 \text{ °C} & \quad \text{Decomposition of ammonium sulfate} \\
(NH_4)_2SO_4 \rightarrow & \quad NH_3 + (NH_4)HSO_4 \\
> 360 \text{ °C} & \quad \text{Vapourisation of ammonium sulfate and reaction with crystal} \\
(NH_4)HSO_4 + 2 Si–O–M & \rightarrow 2 Si–OH + M_2SO_4 + NH_3 \\
M = Na, K
\end{align*}
\]

\(\dagger\) Following mechanical cutting of the crystal, the surface of the cuts is opaque. Acid polishing in mixtures of sulfatic and hydrofluoric acid renders the crystal transparent once more.

### 17 Lead—what is the future?

Lead is an important element and still has many industrial uses. However, there are undoubtedly significant risks associated with excessive exposure to lead either in the home or in the workplace. In recognition of this the Organisation for Economic Cooperation and Development (OECD) signed a ministerial declaration on risk reduction for lead at their meeting in Paris on 20th February 1996. This was the conclusion of a long debate within the OECD on the need to place mandatory restrictions on lead products. The main points in the OECD declaration are:

- Phase out of the use of lead in gasoline except where required for essential or specialised uses where there are no practical alternatives.
- Elimination of exposure of children to lead arising from products intended for use by children.
- Eliminate exposure to lead from food packaging.
- Phase out the use of lead in paint and rust-proofing agents except in cases of essential or specialised uses for which there are no practical alternatives.
- Restrict exposure to lead from the leaching/migration of lead from ceramic ware and crystalware used for food and beverages.
- Restrict the use of lead shot in wetlands.
- Promote the use of alternatives to lead weights used for fishing in shallow water.
- Reduce lead levels in drinking water.
- Reduce the levels of lead in occupational environments.
- Limit lead in air emissions.
- Establish strategies to abate significant exposures to lead arising from the historic use of lead-containing materials in buildings.

These measures are not inconsistent with the views of Simms\(^40\) who proposed a scientific basis for regulating lead contamination and there is no reason to believe that their implementation will not result in a significant reduction in exposure to lead. This will be manifested by decreases in the average blood lead levels in the general population and a reduction in the numbers at risk to elevated blood lead levels. Fig. 10 summarises the findings of the third National Health and Nutrition Examination Study (NHANES III) carried out to assess the health and nutritional status of the US population. The previous study, NHANES II, carried out from 1976–1980 reported an average blood lead level of 12.8 μg dl\(^{-1}\). The initial results of NHANES III, which covers the period from 1988–1991 has found that the average blood lead level in the US population is now 2.8 μg dl\(^{-1}\).

The decline is significant across all age groups. The largest decline was in the 6–15 years age group with large reductions also found in the most sensitive age group, 1–5 years where the average blood lead level decreased from 14.9 to 3.6 μg dl\(^{-1}\). It is estimated that approximately 1.7 million US children currently have blood lead levels greater than 10 μg dl\(^{-1}\), the intervention level set by the Centers for Disease Control. This is considerably less than the number claimed by environmental pressure groups. Surely the most significant finding of this study is that these striking reductions in blood lead levels have been achieved despite an increase in lead consumption from 4.8 to 5.26 kg per person over the same period. This clearly demonstrates that lead can be used safely in modern society. These findings are supported by recent data from Australia. In 1993 the National Health and Medical Research Council
Organization have finally released their position document on the International Labour Organisation and the World Health Organization that neurotoxic effects and to induce impairment of the central nervous system may in the near future result in these effects challenging cancer as a prime focus of toxicity research on lead. The technology to be used for reducing blood lead levels, the growing awareness of the potential of chemicals such as lead to have implications in the workplace. Although significant advances have been made in reducing blood lead levels, the sole option for preventing low-level lead effects in therapy are neither appropriate nor logistically feasible for the treatment of people who have been exposed to low levels of lead. The implementation of OECD recommendations should provide further impetus to a general reduction in blood lead levels. In addition, further reductions in the permissible concentrations of lead in ambient air will be implemented. In the EU, this is currently 2 µg m\(^{-3}\). However, the WHO working group on inorganic air pollutants has recently recommended a fourfold reduction to 0.5 µg m\(^{-3}\) and the UK Department of the Environment has recently proposed that such a limit be implemented. Bearing in mind that the upper limit for lead of nonanthropogenic origin in blood is 5 µg dL\(^{-1}\), such a proposal would ensure that children would have levels of less than 10 µg dL\(^{-1}\), the level at which the WHO considers the onset of adverse effects to begin.

Since traditional medical approaches such as chelation therapy are neither appropriate nor logistically feasible for the treatment of people who have been exposed to low levels of lead, the sole option for preventing low-level lead effects in millions of young children is to preclude further exposure. Similar arguments apply to adults. This will have important implications in the workplace. Although significant advances have been made in reducing blood lead levels, the growing awareness of the potential of chemicals such as lead to have neurotoxic effects and to induce impairment of the central nervous system may in the near future result in these effects challenging cancer as a prime focus of toxicity research on chemicals.

The International Program on Chemical Safety (IPCS), a joint venture of the United Nations Environmental Program, the International Labour Organisation and the World Health Organization have finally released their position document on lead. This document addresses most of the major health impacts of lead and the lead industry accepts that it presents a thorough and balanced view. It outlines a number of areas for future research as follows:

- To define the health significance of biochemical changes associated with exposure to lead, with particular attention to alterations associated with blood lead concentrations of the order of 15 µg dL\(^{-1}\) or less.
- To define the bioavailability of lead from various sources and to establish the relationship between exposure (source and speciation) and body burden.
- To define the influence of host-related factors (particularly nutrition) affecting absorption and distribution of lead.
- To intensify kinetic studies of lead in order to provide an improved database for extrapolation between species.
- To elucidate mechanisms of accumulation and mobilisation of lead from bone with particular attention to the influence of pregnancy and ageing on the kinetics.
- To investigate the pharmacokinetics of lead in pregnancy in relation to transfer of lead to the developing embryo and foetus and factors that mitigate such transfer.
- To determine the effects of pre- and post-natal exposure to lead.
- To improve the definition of paternally mediated effects of lead exposure on the reproductive process and outcomes.

It is apparent that these recommendations address many of the acknowledged deficits highlighted in this review. It is worthwhile noting that the International Lead Zinc Research Organization (ILZRO) has already initiated major research programmes in a number of these areas.

18 References

21 A. Hamilton, Exploring the dangerous trades, Little-Brown, Boston, 1943.

29 ATSDR, Case studies in environmental medicine: lead toxicity, Agency for Toxic Substances Disease Registry, Atlanta, GA., 1990.


33 H. L. Needleman and R. J. Jackson, Pediatrics, 1992, 89, 678.


41 ILZRO, Environmental Update, 1996, 6, 2.

Received, 12th August 1996
Accepted, 19th December 1996

146 Chemical Society Reviews, 1997