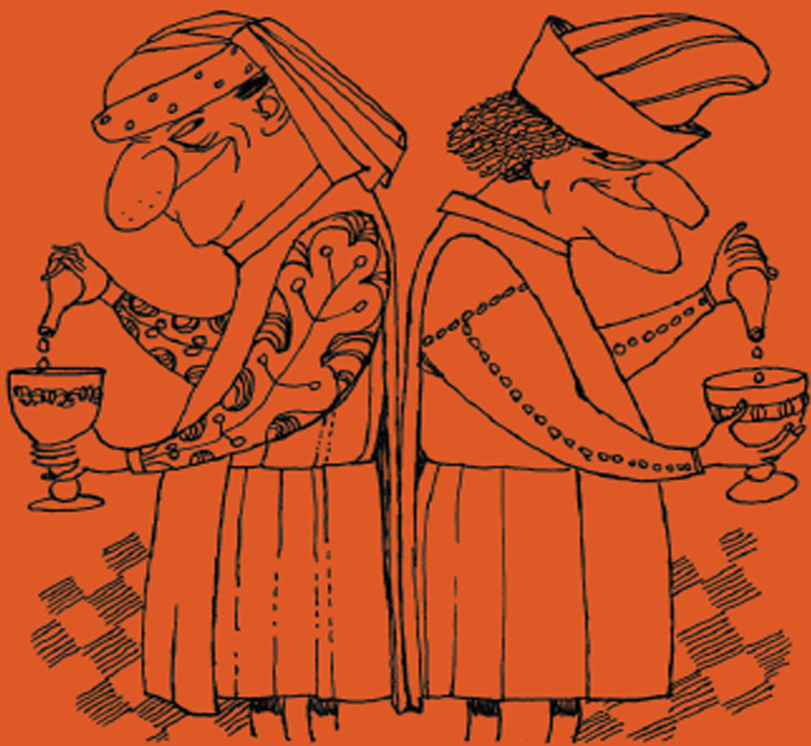
THE CRUMBS OF CREATION

JOHN LENIHAN



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Trace elements in history, medicine, industry, crime and folklore

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Foreword

This book had its origin in a course of lectures which I gave while serving as Regents' Professor in the Chemistry Department of the University of California, Irvine—a stimulating environment which was made all the more agreeable by the kindness and courtesy accorded to me by both staff and students. Mr Michael Purcell suggested that the lectures should be expanded for publication and Miss Nancy Truglio allowed me to make use of the excellent notes which she wrote during the course. I owe a particular debt of gratitude to Professor Vincent Guinn, whose friendship and collaboration, extending over nearly three decades, have much enhanced my knowledge and understanding of trace element chemistry in its widest context.

I have, for an even longer spell of years, enjoyed involvement—more often as a quartermaster than an active participant—in the imaginative and fruitful programme directed by Professor Hamilton Smith of the Department of Forensic Medicine and Science of the University of Glasgow. In the pages which follow I have drawn freely on the published and unpublished research of Professor Smith and of others who have worked with us—notably Dr Ian Dale, Dr David Lyon and Dr Janet Warren.

Chapter 5 contains material which originally appeared in *The Practitioner.* I am grateful to the editor and proprietors of that eminent journal for permission to reproduce it here.

The tasks of gathering and classifying information from a multitude of sources and the drafting of text have made heavy demands on the patience and devotion of many colleagues—especially Mrs May Buchanan, Mr Douglas Craig, Mrs Margaret Tait, Miss Anne Wotherspoon and Mrs Ellen Woodards. I have also enjoyed the privilege of access to the incomparable riches of the Glasgow University Library and to the ever helpful expertise of its staff.

At the University of California, Santa Barbara, my search for information on Drake's Plate (Chapter 7) succeeded through the help of Dr Joseph Boise, University Librarian, and Mr Christian Brun, Head of the Department of Special Collections.

Dr Alan Richardson and Mrs Jean Robertson have read the whole of the text; Professor Guinn and Mr Herbert Soulsby read some of the chapters. I am grateful to these friends for their thoughtful comments.

During the years when this book was in preparation I have been supported by the encouragement and practical help of Mrs Lena Fleming, Professor Agnes Jarvis, Miss Deborah Rogers, Mrs Patricia White and—most of all—my wife.

Several of my earlier writings were illustrated by Mr Jack Fleming, whose witty and elegant drawings added a new dimension to the scientific content. Our collaboration was, to my profound sorrow, ended by his death in 1986. Drawings which he had completed enrich the text of this book—and remind us of what might have been.

I appreciate the care and skill with which the Adam Hilger staff have handled the preparation of this book; in particular, Neville Hankins (commissioning editor) and Neil Robertson (desk editor).

John Lenihan
Glasgow
January 1988

Introduction

God, according to Voltaire, is on the side of the big battalions. The Universe certainly seems to demonstrate this strategy. Almost everywhere the environment is dominated by just a few chemical elements—hydrogen and helium in outer space, oxygen and silicon in the Earth's crust, oxygen and hydrogen in living matter. At the other end of the scale, many elements are found in extremely small concentrations, measured in parts per million (PPM), parts per billion (PPB) or even less. These are the trace elements.

The concept originated during the 19th century. Analytical chemists, when reporting on a sample, would state the relative proportions of its constituents. Any which were present at levels sufficient to be identified but not measured were reported as 'traces'. The first recorded example of this usage is attributed to Faraday. He wrote in 1827 of a process occurring in a blast furnace 'leaving scarcely a trace of slag'. He may have been thinking of a trace as a streak, which is how a small amount of slag would appear on molten metal, but the word was useful in the rapidly-developing science of analytical chemistry—and in other fields also.

In 1876 Mr W E Gladstone, writing (in the *Contemporary Review*) on varieties of religious belief, offered a new simile: 'Like a chemist who, in a testing analysis . . . if he finds something behind so minute as to refuse any quantitative estimate, calls it by the name of "trace".'

As the result of advances in analytical chemistry, particularly during the past 40 years, virtually all of the elements formerly designated as traces can now be accurately measured. Some appear to be of little significance in living systems but others, with which this book is concerned, demonstrate importance out of proportion to their meagre abundance.

We define a trace element as one which is present to a very small extent in a particular environment and which either

(a) by its presence gives significant information,
or
(b) by the expression of its chemical and physical properties exerts a distinctive influence (adverse or advantageous) on its environment.

In the pages which follow, the role of trace elements will be reviewed in relation to several environments.

(i) The geological environment is, for our purpose, the crust, oceans and atmosphere of the Earth. We shall discuss the contribution of trace element analysis to understanding of the end of the dinosaurs, to exploration for minerals, to environmental pollution and to the role of water in human health.
(ii) The biological environment includes all living matter. We shall examine the role of trace elements in plant, animal and human nutrition and in various occupational and environmental hazards to human health.
(iii) In the context of the social environment, we shall review the contribution of trace element studies to the detection of crime—contemporary and historical—and to scholarly activity in art and archaeology.

In trying to identify, among the 90 naturally-occurring elements listed in appendix 1, those which we shall study in this book as trace elements, we can start by excluding 11 which are the most abundant in the tissues of man and the higher animals and plants and may therefore be regarded as bulk elements. They are: hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, sulphur, chlorine, phosphorus, potassium and calcium. Of the remaining 79 elements, we can exclude the six noble gases. These (helium, neon, argon, krypton, xenon and radon) were for many years regarded as completely inert; it is now known that some of them do form compounds—but none of biological relevance. We can also exclude the seven heavy elements (polonium, francium, radium, actinium, thorium, protactinium and uranium) which are invariably radioactive, as they have no stable isotopes.

We are left with 66 elements, all of which are found in the earth's crust and are therefore present in animal and plant tissues—though not always at levels within the reach of existing analytical techniques. These might all be regarded as trace elements. In this book we shall be concerned only with those which are essential for the life of animals (including man) or plants, and a few more which are interesting because of their toxic effects. These restrictions reduce the list to 19: boron, fluorine, silicon, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, molybdenum, cadmium, tin, iodine, mercury and lead.

The study of trace elements has been transformed by great advances in the techniques of analytical chemistry during the past 40 years. The first breakthrough was achieved by the development of neutron activation analysis during and after the Second World War. Many elements become radioactive when exposed to neutron bombardment, usually inside a nuclear reactor. Assay of the radioactivity induced in a sample, which is highly characteristic of the elements contributing to it, forms the basis of an extraordinarily sensitive analytical procedure, applicable to most of the trace elements mentioned in this book. Other techniques, offering comparable or greater sensitivity for many trace elements, have become available more recently and have been used in some of the work described here.

CHAPTER 1

Hair and History

A KING KILLED BY CHEMISTRY?

The King was not happy. As 1685 began, his years of exile and adversity were long gone, he was politically secure, his kingdom was peaceful and prosperous, he had both the inclination and the means to live in extravagant style—but his health was declining. Prevented by an attack of gout from taking his daily walk in St James's Park, he spent more time than usual in his laboratory, distilling mercury (a process favoured by the alchemists in their efforts to make gold) and otherwise dabbling in the sciences of which he was such a notable patron. Charles II is revered today as the founder of the Royal Society—the world's most illustrious learned society—but in his own age he was criticised for spending too much time in his laboratory and not enough in the councils of state.

On Sunday 1 February 1685 his old exuberance returned. He passed the day in his palace at Whitehall in the company of revellers and gamblers, carousing with three of his mistresses and generally enjoying the robust pleasures for which his court was notorious. On the following morning the courtiers noticed that his speech was indistinct and his mind confused. Suddenly he collapsed. His physicians—fourteen of them—argued among themselves while administering unpleasant and useless remedies.

On 6 February the King died. Apart from the inevitable rumours of poison, the cause of his last illness remained obscure for nearly three centuries. In 1961, two American physicians reviewed the evidence and produced a diagnosis of kidney failure, attributable to mercury poisoning; this was quite consistent with the King's well-authenticated history of exposure to mercury vapour in his laboratory.

His physicians argued among themselves.

Seeking further support for their diagnosis, they suggested that analysis of the King's hair might show whether he had absorbed a significant amount of mercury. In 1966, after a broadcast appeal, a viewer in Wales donated a small sample for examination by Dr (now Professor) Hamilton Smith in the Department of Forensic Medicine at Glasgow University.

This relic came from a lock of hair, mounted on a card bearing the words:

> 'This lock of hair was taken from the head of King Charles the 2nd, by the mother of Sir John Jennings Kt, and given to Miss Steele of Bromley by Phillip Jennings Esq. Nephew to the Admiral Sir John Jennings above said 1705'.

The King's hair was found, by neutron activation analysis, to contain 54 PPM of mercury. This is a very high value (about 20 times greater than today's normal level) and gives some support to the long-range diagnosis of the American physicians—although, since it is not known when the lock was cut from the King's head, it is not possible to be confident that he died of mercury poisoning. The investigation does, however, illustrate the use of hair analysis in the study of historical problems. To appreciate the value of this technique we need to know more about the physical and chemical properties of hair.

STRUCTURE AND PROPERTIES OF HAIR

Hair is a fascinating though undervalued material, offering much of interest to workers in medicine, forensic science, environmental hazard control and even history. In these disciplines its usefulness, which cannot always be exploited without difficulty or controversy, depends on several factors:

(1) it records contamination from inside the body (since it is a pathway of excretion for many metals) and from outside, since it traps metallic vapours and dust.
(2) Growing at a fairly uniform rate of about a centimetre a month, it acts as an integrating dosemeter, with a built-in time scale. Blood and urine, though widely used as indicators of exposure to toxic substances, are of limited value for this purpose since they record only recent exposure.
(3) It can be collected quickly and painlessly without specialised skill or equipment and (in contrast to most other tissues) can be stored and transported cheaply without deterioration.
(4) Many trace elements are found at higher concentrations in hair than in other tissues (table 1.1).
(5) It can be analysed with great sensitivity by techniques which are widely available.
(6) It is very durable. Samples from as far back as the 4th century show little change in physical characteristics.

To understand how these properties come about, we need to know something of the physical and chemical structure of the material. Hair, like skin and nail, is composed largely of keratin (a tough protein) and may be regarded as a solid secretion of the skin. Its formation from materials in soft tissue, blood and other body fluids begins in the follicles which cover most of the body. In man there are about 100 000 on the scalp, 10 000 to 20 000 on the face and up to a million on the rest of the body.

A hair consists of four parts, not of equal value or interest to the analyst. The root is embedded in the follicle. The shaft, which emerges through an opening in the skin, has three parts. The cuticle is a structure of overlapping scales, giving protection from mechanical and chemical insults. The cortex, a hollow cylinder which makes up most of the hair, is composed of keratin fibres. The medulla is a central cavity, usually absent in fine hair and not always continuous in coarse hair, as on the scalp. When present, it is filled with fibre-walled cells (which contribute stiffness) separated by air spaces.

Table 1.1 Typical trace element concentration, PPM.

Element	Whole body	Blood	Hair
aluminium	1	0.4	5
arsenic	0.2	0.005	0.5
gold	0.01	0.0001	0.1
bromine	4	5	30
cadmium	0.7	0.005	1
chromium	0.1	0.1	1
copper	1	1	15
mercury	0.2	0.01	2
magnesium	0.3	0.3	40
manganese	0.2	0.05	0.3
nickel	0.01	0.03	3
lead	2	0.2	20
selenium	0.2	0.2	20
titanium	0.2	0.05	4
zinc	33	7	150

The colour of the hair is influenced by the chemical composition of the melanin, a pigment which occurs in the medulla and, to a lesser extent, in the cortex. Hair becomes whiter in old age, partly through loss of pigment and also because the cells in the medulla shrink; the intervening air bubbles then become more numerous and the hair reflects more light.

In man (as in the cat and the guinea pig, though not in most other animals) each hair grows independently of its neighbours; that is why we don't moult. At any time, about 90 percent of the hairs on a human head are growing. The remainder, except for a few at an intermediate stage, are resting. The growth phase lasts for about 900 days and is followed by the resting phase which continues for about 100 days. After that, one of two processes occurs; the root may shrink, allowing the hair to fall out, or a fresh growth cycle may begin.

The major chemical constituents of hair, as of every other tissue, are