GAS SOURCE MASS SPECTROMETRY
OF TRACE LEADS FROM
SUDBURY, ONTARIO

by

TADEUSZ JAN ULRYCH

B.Sc., University of London, 1957

M.Sc., University of British Columbia, 1960

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

PHYSICS

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

August, 1962

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia,
Vancouver 8, Canada.

Date August 28 1962

The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

TADEUSZ JAN ULRYCH

B.Sc., University of London, 1957

M.Sc., University of British Columbia, 1960

MONDAY, AUGUST 27, 1962, at 11:30 A.M.

IN ROOM 303, PHYSICS BUILDING

PUBLICATIONS

1. Kollar, F., Russell, R.D. and Ulrych, T.J.
Precision intercomparisons of lead isotope
ratios: Broken Hill and Mount Isa.
Nature, 187, 754-756, No. 4739, 1960.
2. Russell, R.D., Ulrych, T.J. and Kollar, F.
Anomalous leads from Broken Hill, Australia.
Journal of Geophysical Research, 66, 1495-
1498, No. 5, 1961.

COMMITTEE IN CHARGE

Chairman: F.H. SOWARD

S.D. CAVERS

J.A. JACOBS

F.W. DALBY

D.L. LIVESEY

R.E. DELEVAULT

R.D. RUSSELL

W.F. SLAWSON

External Examiner: R.M. FARQUHAR

University of Toronto

GAS SOURCE MASS SPECTROMETRY OF
TRACE LEADS FROM SUDBURY, ONTARIO

ABSTRACT

The measurement of lead isotope abundances with a gas source mass spectrometer has been limited to lead ores and minerals. This thesis describes a technique by means of which the sample size necessary for a precise gas source analysis has been decreased by more than two orders of magnitude. In this way, the range of minerals which may be studied by means of a gas source mass spectrometer has been greatly extended. No particular effort has been made to analyze very small samples.

The technique which has been developed begins with the evaporation of lead from a mineral to form a mirror. The synthesis of tetramethyllead is completed by the reaction of free methyl radicals with the lead mirror followed by gas chromatographic purification.

The free radical method has been applied to the study of lead isotope abundance variations in the mining district of Sudbury, Ontario. A satisfactory chronological history for this region has not been obtained from the many conventional age determinations that exist. The analysis of lead from various sulphides has yielded lead isotope ratios which are linearly related on a plot of Pb^{207}/Pb^{204} vs. Pb^{206}/Pb^{204} with a slope of 0.131 ± 0.003 . The standard deviation of points from their best straight line is 0.37% of the average Pb^{207}/Pb^{204} value. From these results it is concluded that the linear relationship is the result of just two geological events, which fact simplifies the possible interpretations. The maximum ages for these two events are 2150 ± 50 million years and 1280 ± 50 million years.

Two interpretations of the results are suggested. The first gives ages of 1950 million years and 350 million years for the primary and secondary events. The two events in the second interpretation are considered to have occurred 1600 million years and 950 million years ago. The second interpretation is more easily defended on geological grounds.

The simple relationship of lead isotope ratios which has been observed in the Sudbury district is particularly significant in view of the geological complexity of this region. Thus the technique developed may be expected to have wide application.

GRADUATE STUDIES

Field of Study: Isotopic Studies of Geophysical Importance

Advanced Geophysics J.A. Jacobs

Geomagnetism J.A. Jacobs

Modern Aspects of Geophysics Staff in Geophysics

Introduction to Dynamic Oceanography C.L. Pickard

Advanced Dynamic Oceanography . C.L. Pickard

Related Studies:

Applied Electromagnetic Theory . G.B. Walker

Unit Operations II S.D. Cavers

ABSTRACT

The measurement of lead isotope abundances with a gas source mass spectrometer has been limited to lead ores and minerals. This thesis describes a technique by means of which the sample size necessary for a precise gas source analysis has been decreased by more than two orders of magnitude. In this way, the range of minerals which may be studied by means of a gas source mass spectrometer has been greatly extended. No particular effort has been made to analyze very small samples.

The technique which has been developed begins with the evaporation of lead from a mineral to form a mirror. The synthesis of tetramethyllead is completed by the reaction of free methyl radicals with the lead mirror followed by gas chromatographic purification.

The free radical method has been applied to the study of lead isotope abundance variations in the mining district of Sudbury, Ontario. A satisfactory chronological history for this region has not been obtained from the many conventional age determinations that exist. The analysis of lead from various sulphides has yielded lead isotope ratios which are linearly related on a plot of Pb^{207}/Pb^{204} vs. Pb^{206}/Pb^{204} with a slope of 0.131 ± 0.003 . The standard deviation of

points from their best straight line is 0.37% of the average $\text{Pb}^{207}/\text{Pb}^{204}$ value. From these results it is concluded that the linear relationship is the result of just two geological events, which fact simplifies the possible interpretations. The maximum ages for these two events are 2150 ± 50 million years and 1280 ± 50 million years.

Two interpretations of the results are suggested. The first gives ages of 1950 million years and 350 million years for the primary and secondary events. The two events in the second interpretation are considered to have occurred 1600 million years and 950 million years ago. The second interpretation is more easily defended on geological grounds.

The simple relationship of lead isotope ratios which has been observed in the Sudbury district is particularly significant in view of the geological complexity of this region. Thus the technique developed may be expected to have wide application.

ACKNOWLEDGEMENTS

I find great pleasure in acknowledging the help which I have received from many sources. Particular thanks are due to Dr. R. D. Russell whose guidance and enthusiasm have contributed immeasurably to this study. Dr. W. F. Slawson kindly read the draft of this thesis and made many valuable suggestions. P. H. Neukirchner and J. Lees have helped me considerably with the experimental side of this study. Dr. R. M. Farquhar of the University of Toronto supplied the original spectrograms from which the Toronto results were calculated. E. R. Kanasewich, R. G. Ostic and A. B. Whittles were kind enough to allow me to make use of their unpublished analyses. A. J. Naldrett of Queen's University and A. J. Sinclair generously donated samples for the present research. Dr. D. M. Shaw of McMaster University very kindly analyzed some samples spectroscopically. The facilities provided by the Department of Mining and Metallurgy are gratefully acknowledged. I have received much encouragement in the course of this study from Dr. J. A. Jacobs, my wife and friends and had the pleasure of many stimulating discussions with J. S. Stacey and F. Kollar. Thanks are due to Miss J. Kelly and Miss S. Hanmer who computed the results and to Miss N. Beman who typed this thesis. The work was financed by grants from the Petroleum Research Fund of the American

TABLE OF CONTENTS

ABSTRACT	ii
LIST OF ILLUSTRATIONS	vi
LIST OF TABLES	viii
ACKNOWLEDGEMENTS	ix
INTRODUCTION	1
CHAPTER I LEAD ISOTOPE ANALYSIS WITH THE MASS SPECTROMETER	
Need for isotopic analysis of trace amounts of lead	6
The mass spectrometer ion source	7
The tetramethyllead technique	11
Desirability of the free radical technique	14
CHAPTER II FREE RADICAL PREPARATION AND GAS CHROMATOGRAPHIC PURIFICATION OF TETRAMETHYLLEAD	
The free radical technique	19
Production of free radicals	22
Mirror activity	26
Gas chromatographic technique	29
Theory of gas chromatographic separation	33
Classification of chromatographic theories	36
The Plate theory	40
The Rate theory	46
Predictions from Rate theory	50

CHAPTER III APPARATUS, METHOD AND PRELIMINARY

RESULTS

Production of free radicals and mirror removal	56
Gas chromatographic purification of tetramethyllead	62
Design of suitable chromatographic column	69
The preparation of lead mirrors from various sulphides	80
Procedure for the synthesis of tetramethyllead	85
Preliminary results	86

CHAPTER IV LEAD ISOTOPE ABUNDANCES FROM

SUDBURY, ONTARIO

Introduction	94
Experimental results	100
Interpretations of the Sudbury lead isotope ratios	111

CONCLUSIONS	122
-------------	-----

APPENDIX

The Plate theory in gas chromatography	129
The Rate theory in gas chromatography	135

LIST OF ILLUSTRATIONS

Fig. 1	Vapour pressure of tetramethyllead	16
Fig. 2	Apparatus used by Paneth and Hofeditz to detect free radicals	21
Fig. 3	Diagram of apparatus for gas-liquid chromatography	34
Fig. 4	Classification of types of chromatography	37
Fig. 5	An ideally eluted solute	41
Fig. 6	Relation between number of plates (n), separation factor (α) and fractional band impurity (η)	43
Fig. 7	Definition of band impurity	44
Fig. 8	Graphical representation of the Rate equation in gas-liquid chromatography	49
Fig. 9	Diagram of apparatus for the free radical synthesis of tetramethyllead	57
Fig. 10	Techniques for introducing samples into a chromatographic column	64
Fig. 11	Details of thermal conductivity sensing device	67
Fig. 12	Separations of the reaction products of the pyrolysis of di-tertiary-butyl peroxide	72
Fig. 13	Gas chromatographic separation of tetramethyllead. 1.	75

Fig. 14	Gas chromatographic separation of tetramethyllead. 2.	77
Fig. 15	Diagram of resistance furnace	81
Fig. 16	Trimethyllead spectrum obtained using the free radical technique	89
Fig. 17	Generalized geological map of the Sudbury area	96
Fig. 18	Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads. University of Toronto analyses	99
Fig. 19	Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads. University of British Columbia and University of Toronto analyses	107
Fig. 20	Pb^{208}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads. University of British Columbia and University of Toronto analyses	108
Fig. 21	Histogram of K - Ar and Rb - Sr ages from Sudbury	124
Fig. 22	Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Dominion Reef galenas and for Sudbury sulphides	127
Fig. A1	Three successive adsorption vessels	129
Fig. A2	Elution curve	132
Fig. A3	Material balance in a continuous column	136

LIST OF TABLES

Table 1	Tetramethyllead characteristics	15
Table 2	Reactivity of various metal mirrors with free radicals	30
Table 3	Metal alkyls identified in reactions between the metal mirror and free methyl radicals	32
Table 4	Characteristics of chromatographic columns for the purification of tetramethyllead	78
Table 5	Typical precision of analyses with the free radical and Grignard techniques for synthesis of tetramethyllead	88
Table 6	Lead isotope abundances and description of samples used in preliminary experiments	92
Table 7	Location and geological description of samples from Sudbury, Ontario	101
Table 8	Isotopic analyses of Sudbury leads	104
Table 9	Definition of symbols used in the calculation of the ages of the Sudbury leads	112
Table 10	Values of the parameters t , V_0 and W_0 for some ordinary leads	117

Chemical Society and from the National Research Council of Canada. I would like to express my gratitude for a National Research Council studentship.

INTRODUCTION

The Geophysical laboratory at the University of British Columbia has been actively concerned with the measurement and interpretation of lead isotope abundances during the past four years. The writer joined this laboratory in September 1958 and at that time Dr. F. Kollar and Dr. R. D. Russell were developing a precise gas source mass spectrometer for lead isotope analysis. It became apparent to the writer that the precision of measurement may be enhanced not only by improved instrumentation but also by superior sample preparation. With this in mind he developed a gas chromatographic technique for sample purification which has found immediate application in this laboratory and has been used regularly ever since (Ulrych, 1960). Purity of samples increases the precision in a number of ways. Specifically, the pressure and composition of the gas in the ionization chamber may be easily reproduced allowing precise intercomparison of samples (Kollar, Russell and Ulrych, 1960), and the lower pressures obtained decrease the pressure scattering which has been one of the principal sources of error in gas source measurements of lead (Russell and Slawson, 1962; Richards, 1962a).

Lead isotope variations are measured with the aid of a mass spectrometer, two types of ion sources being used. The gas source technique using tetramethyllead has yielded the

highest precision (Kollar, Russell and Ulrych, 1960) and is a common method for the study of lead minerals. The present technique for preparing tetramethyllead for isotopic analysis is a development of the Grignard synthesis described by Jones and Werner (1918) and first applied in the present form by Collins, Freeman and Wilson (1951). The principle limitations of this procedure arise from the complexity of the semi-micro organic synthesis employed. The amount of sample required depends largely on the particular techniques, smaller samples requiring more elaborate syntheses and demanding a higher degree of chemical skill. With simple equipment it is relatively easy to prepare and purify tetramethyllead from a few hundred milligrams of lead iodide. This is the sample size used at the University of British Columbia for the precise intercomparison of common lead isotope ratios. At other laboratories the same technique has been extended to the 10 milligram range, but not on a routine basis and not with the best precision. Richards (1962b) has substituted the procedure of Gilman and Jones (1950) for the older Grignard synthesis and obtained good results with 40 milligram samples of lead chloride, but the equipment and procedures are quite elaborate. Other experiments in the preparation of milligram amounts of tetramethyllead for isotopic analysis have been reported, but in all cases the precision of the analyses has been unsatisfactory. Thus it

is reasonable to take a figure of 100 milligrams of lead as the required amount of sample to carry out the best isotopic analyses. Although this limitation in sample size is not serious when applied to lead minerals and ores, it prohibits the study of lead isotope abundances in minerals and rocks which contain lead only as a minor constituent.

The solid source technique which has been the only satisfactory one for smaller amounts of lead has some disadvantages. Specifically, surface ionization is a process which is not easily controlled and poor reproducibility of peak heights may result from varying ion efficiencies (Mair, 1958). Often a very large number of spectra have to be recorded. The chemistry involved in preparing samples for analysis by this method requires a high degree of specialization and skill. Most important, the intercomparison technique cannot be used with solid source analysis. This is also true of the method reported by Ehrenberg, Geiss and Taubert (1955) who analyzed milligram quantities of galena directly by heating the sample in the ion source of the mass spectrometer.

With the above considerations in mind, the writer became interested in developing, in a practical form for mass spectrometry, the preparation of tetramethyllead by the reaction of free methyl radicals with metallic lead mirrors. This

would serve two purposes. In the first place, it would extend the range of the tetramethyllead technique to samples which contain lead as a minor constituent. In the second place, it could be a simple technique, reducing the possibility of contamination and adaptable for routine studies.

Preliminary work on the feasibility of this technique was carried out by Surkan (1956), who obtained sufficiently intense ion beams for mass spectrometer analysis from 500 micrograms of lead. Serious contamination problems were encountered, however, and this method was not developed further. Surkan's studies served as a starting point for the present research.

This thesis is concerned with describing a practical procedure which has been developed, consisting basically of three parts:

(i) Volatilization of the lead from a sample in a hydrogen furnace to form a mirror on the inside of a quartz tube.

(ii) Removal of the lead mirror by the action of free methyl radicals to form tetramethyllead.

(iii) Purification of the tetramethyllead by means of

gas-liquid chromatography. (An extension of the writer's earlier work (Ulrych, 1960).)

The thesis is also concerned with the application of the technique to analysis of a suite of pyrites from the Sudbury region of Ontario.

Chapter I of this thesis reviews briefly the two principle types of mass spectrometer ion sources and the standard methods of preparing tetramethyllead for lead isotope analysis. Chapter II describes the necessary theory on which the development of the new technique has been based and Chapter III, the actual apparatus and procedures. Chapter IV contains a study of the genetic history of leads at Sudbury which demonstrates the usefulness of analyses which can be obtained with the free radical technique.

CHAPTER I

LEAD ISOTOPE ANALYSIS WITH THE MASS SPECTROMETER

Need for isotopic analysis of trace amounts of lead

The importance of the study of lead isotope abundances, from a geochemical and a geological viewpoint has been amply demonstrated in recent years. The chief areas of application of lead isotopes have been in geochronology and in the studies of the sources and mode of deposition of lead minerals. In both these areas the additional information obtained by the analysis of leads on a microgram scale has contributed greatly to an understanding of the processes involved and to the formulation of models to explain the observed lead isotope variations.

Probably the first analysis of microgram quantities of lead was carried out by Patterson (1953) who studied leads in meteorites. The important results of this work showed the great potential in studies of this kind. Tilton et al. (1955) carried out the first isotopic analyses from separated minerals of a granite. They found that the granite, considered as a whole, approximated a closed system with respect to uranium and its decay products, but was an open system with respect to thorium and its decay products.

Furthermore, the variation of lead isotope abundances in the granite was related to the important question of lead ore formation. Mair et al. (1960) gained much valuable information from a study of lead isotopes in galena and in the associated minerals, pyrite, pyrrhotite and feldspar occurring near Blind River, Ontario. The most recent example of the significance and importance of trace leads is the study by Murthy and Patterson (1961) of the lead isotopes in rocks and ores of Butte, Montana. Analyses of lead in galenas, pyrites, feldspars and monazites constitute "a valid and serious argument against the suggestion that the ores were derived by differentiation and concentration in the late-stage fluids of a magma".

The examples outlined above and similar considerations have led the writer to the conclusion that although the study of lead isotopes in minerals containing a large proportion of lead is very valuable, the study of minor quantities of lead in other minerals should cast much valuable light on some of the remaining uncertainties associated with lead isotope variations in nature.

The mass spectrometer ion source

Only a brief discussion of the requirements of a mass spectrometer ion source will be presented here. A fuller

treatments are given by Barnard (1953) and Duckworth (1958). The requirements of an ion source for accurate abundance determination may be listed briefly as follows:

(i) The energy spread of the ion beam must be small, particularly in the case of single focussing instruments. This follows from the relation for the radius of ion trajectories, $R \propto (V)^{1/2}$ where V is the accelerating potential, showing that the spread of energy of ions about the value V , will, unless limited, impair resolution.

(ii) The ion beam is required to be stable for accurate measurement since the various isotopes are not measured simultaneously.

(iii) The ion beam should be well collimated. In first order focussing instruments the image formed by the ion beam at the focal plane is widened by $R\alpha^2$, and therefore α , the half angle of divergence from the source must be small.

(iv) The ion beam should be sufficiently intense to allow accurate measurement. Statistical considerations alone require a signal at least as large as

$$\frac{1.6 \times 10^{-15}}{\sigma^2 t} \text{ amperes where } \sigma \text{ is the standard deviation}$$

expressed as a percentage and t is the time of measurement in seconds.

(v) The ion source should not introduce mass discrimination.

(vi) The method of introducing the samples into the ion source should be simple.

(vii) The ion source should be free from contamination and memory effects.

Because of the first two of the requirements, such devices as the arc, spark, gas discharge or the field emission source cannot ordinarily be used with single focussing instruments. The two types of ion source which are most commonly used for isotope abundance determinations are the electron bombardment and the surface ionization sources.

The electron bombardment source, first introduced by Dempster (1918), is used in a gas source mass spectrometer. Samples are introduced either in the form of a solid which is placed in an oven located in the source, as in the case of lead iodide, or in the form of a vapour through a gas leak, as in the case of tetramethyllead. The vapour is ionized by a monoenergetic beam of electrons emitted from an incandescent filament. Serious disadvantages of this type of source are that ionization is neither selective nor efficient. A very important advantage of this source is realized in that the sample is introduced as a vapour.

Sample handling is, then, very convenient and the technique of sample intercomparison, which has helped to improve the precision of lead isotope analyses considerably (Kollar, Russell and Ulrych, 1960) may be used.

Solid samples may be analyzed in a mass spectrometer in two ways; firstly, by the evaporation of a solid with subsequent ionization by an electron beam, as mentioned above and secondly, by direct evaporation from a heated filament. Because of the efficiency of ionization, this technique is particularly suitable for the analysis of microgram quantities and depends on the fact that when a substance is evaporated from a heated surface, there is a probability that it will do so as a positive ion. The actual processes occurring on the surface of a heated filament are not well understood and the best chemistry for a particular element has to be found by experiment. Beynon (1960) points out the critical nature of the chemical form of the sample. In measurements with caesium, the ion beams produced by the evaporation of caesium sulphate and caesium chloride differed by a factor of 10^4 . In the case of lead, impurities in the sample have a considerable effect on the ionization efficiency (Marshall and Hess, 1960).

Compared to the electron bombardment source, the surface ionization source offers both a disadvantage and an advantage. Owing to the necessity of breaking vacuum or of using vacuum

locks, and to the varying ion efficiencies, the technique of sample intercomparison cannot be used. The advantage of this source, however, lies in the fact that it is the only source which has so far been used for the accurate analysis of a few microgram quantities of lead.

The tetramethyllead technique

The study of lead isotope abundances using the vapour of tetramethyllead was first carried out by Aston (1933) who used the discharge in the vapours in a discharge tube. In his extensive studies of the isotopic composition of lead, Nier (1938, 1939) used a method in which lead iodide was evaporated in the vacuum system of a gas source mass spectrometer. This technique is still preferred by some workers. Owing to the time consuming sample handling involved in this method, however, Collins, Freeman and Wilson (1951) turned back to a tetramethyllead technique.

The standard method of preparing tetramethyllead and the interpretation of the spectrum has been described in detail (Diebler and Mohler, 1951; Collins, Farquhar and Russell, 1954). Briefly, the method consists of the reaction between a Grignard reagent and lead chloride (where the term Grignard reagent refers to any solution of an alkyl magnesium halide in ether). Most often, the Grignard reagent used is methyl magnesium bromide. The reaction

probably proceeds in several steps (Coates (1960)).

The first step is probably the production of dimethyllead.

Dimethyllead, like all dialkyl lead compounds, is extremely unstable and disproportionates mainly to hexamethyldilead and metallic lead.

The hexamethyldilead then decomposes into tetramethyllead and free metallic lead, the overall reaction taking place according to the expression

The tetramethyllead is obtained in an ether solution and it is necessary to obtain it in a relatively pure form for mass spectrometer analysis. The separation has usually been effected by a crude distillation followed by a second distillation under vacuum in the mass spectrometer sample line. With increased precision of measurement, more exacting separation became necessary and this was accomplished

using gas-liquid chromatography (Ulrych, 1960).

One of the disadvantages of the Grignard reaction is that only half of the lead is converted into tetramethyllead. Another disadvantage is that, because of the complexity of the synthesis, recovery of small amounts of tetramethyllead is very difficult and this method cannot be used with microgram quantities of lead. Although this is not a restriction in the case of lead minerals, like galena, minerals which contain lead as a minor constituent cannot be analyzed using this method. In the case of pyrite for example, which might typically contain 100 parts per million of lead, approximately 100 grams would have to be processed for adequate analysis in the mass spectrometer.

The loss of half of the lead may be avoided by preparing tetramethyllead using the reaction between methyl lithium and a suspension of lead chloride in ether which also contains methyl iodide (Gilman and Jones, 1950; Richards, 1962b).

The reaction is thought to proceed as follows:

The overall reaction may be written

The disadvantage of the Grignard synthesis, that microgram quantities of lead cannot be used, is also present in this method.

The properties of tetramethyllead are summarized in Table 1 and Fig. 1.

Desirability of the free radical technique

The methods used for preparing samples for mass spectrometer analysis for either the gas or solid source involve the use of micro chemistry and because of their relative complexity require skill in analytical chemistry. The technique used for preparing tetramethyllead for analysis in the gas source mass spectrometer suffers from the severe limitation, discussed above, of being applicable only to lead ores and minerals. The types of minerals which are of interest in lead isotope studies differ enormously in their lead content. They may be roughly divided into three classes.

The first class comprises those minerals which contain lead as a major constituent. The majority of lead isotope

Table 1. Tetramethyllead characteristics.

Colourless, very poisonous liquid.

Non polar.

Soluble in most organic solvents, insoluble in water.

Molecular weight	267.35
Melting point	-27.5°C.
Boiling point	110°C. (Decomposes slightly at this temperature.)
Specific gravity.	1.9952.
Refractive index.	1.5128.
Molar refraction.	40.18.
Specific heat.	0.181 cal. gm. ⁻¹ deg. ⁻¹
Heat of vapourization.	9075 cal. per mole
Heat of formation.	32.6 Kcal. per mole for gas. 23.5 Kcal. per mole for liquid
Molal entropy at 298.16°K.	100.48 $\pm$ 0.2 cal. deg. ⁻¹ (Ideal gas at 1 atm.)
Heat of reaction at constant volume.	-884.8 Kcal. per mole
Heat of reaction at constant pressure.	-886.9 Kcal. per mole

(Kaufman, 1961)

(Handbook of Chemistry and Physics, 42nd. ed., 1960-61)

Fig. 1. Vapour pressure of tetramethyllead.

values reported in the literature have been obtained from galena samples.

Minerals containing several hundred micrograms of lead constitute the second group. This is a large class, and is comprised of minerals such as pyrite, pyrrhotite and marcasite among common lead minerals, and sphene, monazite and zircon among minerals containing uranium.

The third class is made up of materials which contain a few micrograms of lead, such as quartz, perthite, eclogite and others.

The techniques used for the analysis of lead isotope abundances from these three classes of minerals have been briefly mentioned above. The leads contained in the minerals of the first class are analyzed using both the gas and the solid source methods. The lead isotope abundances of the lead in the second class could, prior to the free radical technique, only be determined by means of the surface ionization method. The lead in minerals of the third class can be analyzed solely by means of the solid source technique.

The Geophysical laboratory at the University of British Columbia is equipped with two gas source mass spectrometers. The precision which has been obtained using tetramethyllead and the technique of sample intercomparison

is of the order of 0.1%. Up to the present time it has only been possible to determine lead isotope abundances in lead minerals. The free radical preparation of tetramethyllead is designed to extend the range of minerals which may be studied using gas source mass spectrometry without loss of precision.

CHAPTER II

FREE RADICAL PREPARATION AND GAS CHROMATOGRAPHIC PURIFICATION OF TETRAMETHYLLEAD

The free radical technique

The synthesis of tetramethyllead in the method developed occurs through the action of free methyl radicals on a lead mirror. A brief description of the principles involved is therefore in order.

A free radical is defined as a neutral molecule possessing an unpaired electron. This electron gives rise to an unbalanced electron spin and produces a magnetic moment. Free radicals thus exhibit paramagnetism, a property which is often used for physical demonstration of their existence. Organic free radicals may be divided into two classes.

(i) Stable radicals of long life of the Gomberg type in which a carbon atom is attached to large, usually aromatic groups. An example of this type is triphenyl methyl.

(ii) Short lived highly reactive radicals as phenyl, ethyl and methyl. These radicals are highly energetic, extraordinarily reactive and undergo some chemical change very readily in order to satisfy their valency requirements.

The existence of free alkyl radicals was first

demonstrated by Paneth and Hofeditz (1929) by means of the reaction of the radicals with a metallic mirror. The technique used by Paneth and his co-workers is of interest here because it suggested the idea for the method which has been developed. The apparatus used is shown in Fig. 2.

A specially purified stream of hydrogen at a pressure of 1 or 2 millimeters of mercury was passed through a cooled trap containing tetramethyllead, where the hydrogen was saturated. The flowing tetramethyllead vapour was decomposed at one end of the tube with the aid of a furnace forming a lead mirror on the walls of the tube.

If the mirror was cooled and heat was supplied upstream of the mirror, it gradually disappeared, the rate of removal depending on the distance separating the heated zone and the mirror. Following tests to show that the removal of the mirror was not due to thermal effects of the heated hydrogen, Paneth and Hofeditz concluded that the mirror was removed by the action of free methyl radicals according to the reaction

Fig. 2. Apparatus used by Paneth and Hofeditz to detect free radicals.

Production of free radicals

Free radicals are most commonly produced from the dissociation of organic compounds. There are two possible modes of fission of covalent bonds called homolysis and hterolysis and these occur in the following manner:

where A and B are atoms or groups of atoms. The homolytic reaction is characterized by the production of neutral fragments each possessing an unpaired electron. Thus, by definition, this reaction proceeds through the formation of free radicals. Since two neutral fragments are produced, the energy which has to be supplied is equal to the bond dissociation energy. The second reaction involves the production of two ions of opposite charge and sufficient energy in excess of the bond dissociation energy must be supplied to overcome the electrostatic forces. In gases, large separations of ions and radicals are possible and the excess energy necessary to separate the ions is large. The total energy required for the production of ions is therefore much greater than that required for the production of radicals and the homolytic reaction is favoured. The opposite is true for reaction in solution because of energetic advantages

of the heterolytic reaction.

The main considerations in the choice of a source of free radicals in the present case are twofold. On the one hand, the yield of free radicals must be quantitative, on the other hand, the reaction must not be complicated by the presence of unwanted radicals. Quantitative yields of free radicals may be produced by three mechanisms: pyrolysis, photolysis and electrical discharge.

In pyrolysis, dissociation occurs when the thermal energies of the molecules exceed their bond dissociation energy. This method has been widely used since 1933 when it was shown that free methyl radicals could easily be obtained in quantity by heating azomethane to 400° C. (Leermakers, 1933). Rice (1934) showed that at temperatures of 800° C. or higher, the pyrolysis of vapours of a whole range of stable organic compounds yield the simple alkyl radicals methyl and ethyl. The most important sources of methyl free radicals are di-tertiary-butyl peroxide, the azoalkanes and metallic alkyls. For reasons which are discussed below, di-tertiary-butyl peroxide has been used throughout this work.

The production of free radicals by the photo-dissociation of molecules has been recognised since the

work of Norrish, Crone and Saltmarsh (1934). The advantage of this source, namely the ease of controlling the production of free radicals, is offset by the experimental difficulty of making sources capable of producing more than 1/100 of a mole of radicals per hour steadily (Trotman-Dickenson, 1959). Preliminary experiments by the writer on the photolysis of acetone vapour showed that, unless very strong lamps are used, a quantitative yield of free radicals is not readily obtained.

The third source which suggests itself, the electrical discharge, occurs as one of two fundamentally different types, the silent or non-disruptive and the disruptive discharge. The main effects involved are thermal, corresponding to localised heating to 1500°C or higher (Steacie, 1954). Both types are known to produce free radicals, but because of their violent nature, the situation is complicated by the production of many different types of radicals and atoms with the consequent contamination of the required reaction products.

An efficient source for the production of free methyl radicals from the point of view of high radical yield, absence of interfering radicals and a low temperature of dissociation is the pyrolysis of di-tertiary-butyl peroxide. The principal products of the gas phase thermal decomposition

of di-tertiary-butyl peroxide are ethane and acetone. Other products of the decomposition are methyl ethyl ketone, higher boiling ketones and methane.

The stoichiometry of the reaction (Benson, 1960) may be represented by

The following steps have been proposed to account for the reaction products (Benson, 1960).

The presence of free methyl radicals in the pyrolysis of di-tertiary-butyl peroxide has been shown by Bell et al. (1951) who isolated large quantities of formaldoxime when the pyrolysis occurred in the presence of excess nitric oxide. The variation of free radical concentration with temperature is shown by the steady state calculations of Benson (1960).

Di-tertiary-butyl peroxide at 0.01 atmosphere pressure

Temperature	100°C	200°C	300°C
Pressure of (CH ₃) in mm Hg	1.3x10 ⁻⁶	4x10 ⁻⁴	0.017

At a convenient temperature for experimental purposes the concentration of free methyl radicals is large. A great advantage of di-tertiary-butyl peroxide as a source from the point of view of contaminating products and mirror removal is the apparent slowness of attack of methyl radicals on di-tertiary-butyl peroxide itself. This results in a marked stability with respect to chain decomposition.

Mirror activity

The exact mechanism of mirror removal by free radicals is unknown. It may be supposed that the radical, owing to

its unpaired electron, forms a covalent bond with the metal atom. Waters (1948) explains the removal of a mercury mirror by methyl radicals through the formation of a covalent organo-metallic compound in the following manner:

This type of reaction also occurs when carbon dioxide is chemisorbed onto a surface.

The formation of tetramethyllead presumably also occurs in a similar manner, a lead atom forming covalent bonds with four radicals. It is not known, however, whether the formation of a tetramethyllead molecule occurs by the summation of four lead monomethyls on the metal surface, or by some other process. A possibility is the formation of dimethyllead which, being, extremely unstable, disproportionates in a manner similar to the process occurring in the Grignard reaction described previously.

Paneth and Lautsch (1931) concluded that at reactive metal surfaces a radical is held at the first collision. When a sufficient number of these have diffused in an adsorbed state to the same metal atom, definite chemical compounds are formed, and if volatile, are carried away by the gas stream. Experiments have also shown that on inactive surfaces, such as glass or iron mirrors, only a

thousandth of the radicals colliding with the surface become attracted and are then converted to inactive hydrocarbons. The activity of a reactive mirror is dependant upon several factors. Rice and Rice (1935) cite the following:

(i) Traces of oxygen in the reaction tube may completely deactivate the surface of the mirror. Oxides, therefore, presumably do not react. An exception is tellurium oxide which is volatile and may sublime off leaving a clean metal surface.

(ii) Rapid cooling of the mirror deactivates the mirror by the formation of minute traces of gummy substances which are deposited on the mirror.

(iii) Impurities in the organic compound which is used as the source of free radicals deactivate the mirror.

(iv) Temperature of the mirror controls the rate of mirror removal considerably. In some cases, mirrors will be removed only at elevated temperatures; in other cases, the best results are obtained at room temperature.

The reasons for the reactivity of such metals as lead, bismuth and zinc, and the apparent inertness of gold, silver and magnesium to free radical attack are not well understood. Presumably, such factors as the energy of the metal lattice and the bond dissociation energy of the respective organo-

metallic compound play important roles.

The types of metals which react with free alkyl radicals, and the organo-metallic derivatives which have been identified are given in Tables 2 and 3. A very rough rule based on the data in these tables would suggest that those metals which possess stable, volatile and relatively simple alkyl products will react with free alkyl radicals.

Gas chromatographic technique

For purposes of analysis, lead is admitted into the mass spectrometer in the form of tetramethyllead vapour. Whether tetramethyllead is prepared by the standard method using the Grignard reaction, or by the free radical method which has been developed, it is associated with large amounts of impurities. In the former case, the impurities consist of ether and in some instances water, while in the latter, they consist of the reaction products of the thermal dissociation of di-tertiary-butyl peroxide. For precise analysis it is essential that tetramethyllead be admitted in a pure form. By far the best method from the point of view of purity and experimental facility which can be employed for this purpose is gas-liquid chromatography. With this in mind, the writer developed a technique for the chromatographic purification

Table 2. Reactivity of various metal mirrors with methyl radicals. (after Steacie, 1954)

Metals which react with (but are not necessarily removed by) methyl radicals.

<u>Metal</u>	<u>Symbol</u>
Antimony	Sb
Arsenic	As
Beryllium	Be
Bismuth	Bi
Cadmium	Cd
Calcium	Ca
Iodine	I
Lanthanum	La
Lead	Pb
Lithium	Li
Mercury	Hg
Potassium	K
Selenium	Se
Sodium	Na
Tellurium	Te
Thallium	Tl
Tin	Sn
Zinc	Zn

Table 2. (cont'd)

Metals which do not react with methyl radicals.

<u>Metal</u>	<u>Symbol</u>
Cerium	Ce
Copper	Cu
Gold	Au
Iron	Fe
Magnesium	Mg
Silver	Ag

Table 3. Metal alkyls identified in reactions between the metal mirror and free methyl radicals (Benson, 1960).

Metal	Symbol	Number of isotopes	Compound
Antimony	Sb	2	$\text{Sb}(\text{CH}_3)_3$ $\text{Sb}_2(\text{CH}_3)_4$
Arsenic	As	1	$\text{As}(\text{CH}_3)_3$ $\text{As}(\text{CH}_3)_4$ $\text{As}(\text{CH}_3)_5$
Beryllium	Be	1	$\text{Be}(\text{CH}_3)_2$
Bismuth	Bi	1	$\text{Bi}(\text{CH}_3)_3$ $\text{Bi}_2(\text{CH}_3)_4$
Iodine	I	1	ICH_3
Mercury	Hg	7	$\text{Hg}(\text{CH}_3)_2$ $\text{Hg}_2(\text{CH}_3)_2$
Selenium	Se	6	$\text{Se}(\text{CH}_3)_2$
Tellurium	Te	8	$\text{Te}(\text{CH}_3)_2$ $\text{Te}_2(\text{CH}_3)_2$
Zinc	Zn	4	$\text{Zn}(\text{CH}_3)_2$

of tetramethyllead obtained from the Grignard reaction (Ulrych, 1960) and extended it for application to the present problem.

Before looking at the theory of the chromatographic separation it is well to consider some of the general aspects of gas-liquid chromatography. The main features of this method are shown in Fig. 3. The apparatus embodies a column which can be a straight, U shaped, or coiled tube, containing a suitable inert, size-graded solid which acts as a solid support for the stationary phase. The stationary phase is a liquid possessing a very low vapour pressure at the temperature of the experiment. A small sample of the volatile mixture to be separated is introduced into the top of the column. The components of the mixture are transported through the column in a vapour phase by an inert gas referred to as the eluent or the carrier gas. Because of their different physical properties, the constituents pass through the column at different rates and emerge from it individually. The composition of the effluent can be analyzed quantitatively by a detector sensitive to some property of the vapours, usually the thermal conductivity.

Theory of gas chromatographic separation

The efficiency of separation of a compound composed of two solutes depends on two factors, the column efficiency

Fig. 3. Diagram of apparatus for gas — liquid chromatography
(after Keulemans, 1957).

and solvent efficiency.

The column efficiency is concerned with the broadening of an initially compact zone of solute as it progresses through the column. It is usually expressed in terms of the height equivalent to a theoretical plate which is primarily a function of the column dimensions and operating conditions and depends only in a lesser way on the properties of the solvent and solute. The solvent efficiency, sometimes referred to as the separating factor, is defined as the ratio of the times taken by the peak maximum to travel through the column and depends on the distribution, or partition, coefficients of the respective components. It is thus a function of the properties of the solute and solvent and the column temperature. The partition coefficient k is defined by:

$$k = \frac{\text{amount of solute per unit volume of stationary liquid phase}}{\text{amount of solute per unit volume of moving phase}}$$

The processes occurring in a chromatographic column such as diffusion and mass transfer between two phases may be accurately expressed in mathematical terms by assuming that the column is homogeneous on the macroscopic scale. The main phenomena of solute transport through the column are then described by a one dimensional differential equation (Keulemans, 1957), which is developed in the Appendix. For an

exact description of the prevailing states and processes, the mathematics involved become prohibitive and certain simplifications are introduced which lead to theories of limited validity. The theories nevertheless provide explanations of the various chromatographic phenomena.

The simplifications which are introduced are concerned with two factors. The first of these is the linearity or non-linearity of the distribution isotherm. Fig. 4 shows four possible conditions. Cases 1 and 4 show a linear isotherm and consequently a constant partition coefficient. Cases 2 and 3 are examples of non-linearity. The second factor is the ideality or non-ideality of the conditions in the chromatographic column. Ideal chromatography assumes that processes involved are thermodynamically reversible, that equilibrium is achieved instantaneously and that longitudinal diffusion and similar processes are negligible (Keulemans, 1957). Four combinations of the above two factors are possible giving rise to the four theories of gas chromatography.

Classification of chromatographic theories

(1) Linear ideal chromatography

This is the simplest case possible and the requirements for an effective separation may be conveniently found in mathematical terms. Fig. 4-1 shows the situation in this

TYPE OF
CHROMATOGRAPHY

1
Linear
Ideal

2
Non-linear
Ideal

3
Non-linear
Non-Ideal

4
Linear
Non-ideal

TYPE OF
ISOTHERM

Concentration of solute
in moving phase = X,
in stationary phase = Y

SHAPE OF
SOLUTE BAND

Fig. 4. Classification of types of chromatography (after Martin).

case. The retardation of the solute depends on the product of the partition coefficients and the ratio of the amount of the phases present. Because of the linearity of the isotherm the shape of the band remains unchanged during passage through the column.

(ii) Non-linear ideal chromatography

Fig. 4-2 depicts the existing conditions. Processes occurring in this case are of importance in liquid adsorption chromatography. In this case, non-linearity of the isotherm plays an important part, but ideality may still be assumed. As shown, the elution bands show marked tailing due to adsorption, the front being usually steep. Owing to the interaction of solutes, a rigorous mathematical treatment for the case of more than one solute is not possible.

(iii) Non-linear non-ideal chromatography

This is a very difficult case to express mathematically. The bands are diffuse and neither the tail nor the front is sharp. Fig. 4-3 portrays the situation. Adsorption chromatography with a moving phase belongs to this class.

(iv) Linear non-ideal chromatography

This method is depicted in Fig. 4-4. The bands are broadened in a symmetrical manner during elution through the column and approach a Gaussian distribution. These conditions are of particular importance in the case of gas-liquid

chromatography and since this is the type of chromatography with which the writer is concerned, this case only will be dealt with in the subsequent discussion.

One can use two methods of approach to obtain a mathematical description of the prevailing conditions. The first method, called the Plate theory (Martin and Synge, 1941) is based on a consideration of the column as a discontinuous medium and the treatment is analogous to that of batch distillation where the distillation column is considered to be built up of equivalent plates. The second method considers the column to be a continuous medium and takes into account such processes as diffusion and mass transfer. The approach is known as the Rate theory (Van Deemter, Zuiderweg, and Klinkenberg, 1956).

Both theories are presented here briefly and the theoretical development is summarized in the Appendix. The relationships developed in each theory are particularly valuable in an understanding of the expected separation and the processes acting. The formulae developed according to the Plate theory are used by the writer in a subsequent chapter to calculate the number of theoretical plates of the column used and the degree of separation achieved between tetramethyllead and the associated impurities. The expression derived by the application of the Rate theory on the other hand, allows the contribution of the various processes acting such as

diffusion, mass transfer, gas velocity, etc., to be readily understood.

The Plate theory

The Plate theory is a good approximation to the conditions actually existing in a chromatographic column. The assumptions involved in developing the formulae listed below and derived in the Appendix are:

- (i) The distribution isotherm is linear;
- (ii) The two phases in the column are in equilibrium at all times;
- (iii) The whole sample is admitted into the first plate.

Fig. 5 shows the ideally eluted peak. I is the sample injection point and O represents the exit point of air which does not react with the stationary liquid used. Retention times or volumes with respect to the peak maximum, tail or front are measured from I. Apparent retention times or volumes are measured from O.

The quantities shown in Fig. 5 are defined as follows:

w_b or w = peak width at base, AB

w_h = peak width at half height, CD

w_i = peak width at inflection points, EF

d = distance from the injection point to the centre of the eluted peak, IG.

Fig. 5. An ideally eluted solute (after Keulemans, 1957).

The elution curve approaches a Gaussian distribution for a large number of plates (greater than one hundred) and the equation for the curve may be written as:

$$x_n = \frac{e^{-v} v^n}{n!}$$

where n = total number of plates

v = effective plate volume

$$x_n = \frac{\text{concentration of solute in gas phase at plate } n}{\text{concentration of solute in gas phase at plate } 1}$$

The number of plates and hence the height equivalent to a theoretical plate may be conveniently calculated by use of the following formulae (Appendix):

$$n = \left(\frac{4d}{\omega} \right)^2$$

$$\begin{aligned} \text{H.E.T.P.} &= \text{height equivalent to a theoretical plate} \\ &= \frac{\text{column length}}{n} \end{aligned}$$

Glueckauf (1955) has treated the subject of the requirements for an "analytical separation". Fig. 6 shows the graphical representation of the mathematical expression derived by Glueckauf. The figure gives the relationship between the separation factor or relative volatility α , the number of plates required and the fractional band impurity. The latter is defined according to Fig. 7.

Figure 6. Relation between number of plates (n), separation factor (α), and fractional band impurity (η). (After Glueckauf, 1955).

$$\eta \approx \eta_A = \eta_B = \frac{\Delta m_B}{m_A} = \frac{\Delta m_A}{m_B}$$

Fig. 7. Definition of band impurity, η .

m_A is the number of moles of component A in solute

m_B is the number of moles of component B in solute.

If the cut is made such that the fractional impurity in both bands is equal:

$$\eta_A = \frac{\Delta m_B}{m_A - \Delta m_A} = \eta_B = \frac{\Delta m_A}{m_B - \Delta m_B}$$

since

$$m_1 \gg \Delta m_1, \quad \eta = \frac{\Delta m_A}{m_B} = \frac{\Delta m_B}{m_A}$$

Fig. 6 is used in a subsequent section to determine the impurity in the separated tetramethyllead sample.

The assumption that all the sample has been injected into the first plate leads to symmetric elution peaks. In practise, however, elution peaks are not always symmetric, the leading edge being steeper than the tail. Other factors, such as longitudinal diffusion are not considered in the plate treatment and consequently it is difficult to visualize the actual processes which are encountered in the chromatographic column.

A mathematical expression which permits the evaluation of the effects of certain parameters on the performance of the column has been developed by Van Deemter, Zuiderweg and

Klinkenberg (1956). The approach used is known as the Rate theory.

The Rate theory

The Rate theory attempts to explain the phenomena of band broadening by using a kinetic approach. The three major factors which combine in broadening an initially narrow band of solute as it moves through the column are:

(i) The non-uniformity of flow of the mobile phase.

A microscopic consideration of the column shows that the packing material is not uniform. Variations in particle diameter occur and the differences in shape of the individual particles lead to many different paths for the mobile phase. Thus, variations in gas velocity and in direction of flow occur along the column. These variations cause a spread in the residence time of the molecules of the solute, resulting in band broadening. By analogy with the diffusion which occurs in turbulent flow, this process is termed eddy diffusion.

The eddy diffusion may be characterized by an eddy diffusion coefficient $E = \lambda u d_p$

where u = linear gas velocity

d_p = particle diameter

λ = dimensionless measure of packing irregularities

(ii) Molecular diffusion of solute molecules

Since the axial component either increases or decreases the rate of transport of solute molecules, band broadening results. Molecular diffusion in the gas phase is far more pronounced than in the liquid phase and may be expressed by:

$$\text{Molecular diffusion} = \gamma D_{\text{gas}}$$

where D_{gas} is the diffusivity in the gas phase

and γ is a correction for the tortuosity of the channels.

Eddy diffusion and molecular diffusion are usually combined to give the effective longitudinal diffusivity.

$$D_{\text{eff}} = \gamma D_{\text{gas}} + \lambda u d_p$$

(iii) Finite rate of mass transfer

Owing to resistance to mass transfer, equilibrium between phases is not attained instantaneously. Consequently, the solute molecules may either travel ahead or behind the band according to whether they fail to go into solution or are slow in entering the gas phase. This effect results in band broadening.

The expression for this effect has been shown by Van Deemter, Zuiderweg and Klinkenberg (1956) (Appendix) to be of the form:

$$\frac{8}{\pi^2} \frac{k'}{(1 + k')^2} \frac{d_f^2}{D_{liq}} u$$

where k' is the extraction coefficient and is equal to the partition coefficient multiplied by the ratio of the volume fractions of liquid and gas in the column, $k' = k \frac{F_{liq}}{F_{gas}}$

D_{liq} is the diffusivity in the liquid phase and d_f is the liquid film thickness.

The three contributions to band broadening may now be combined to give the expression for the height equivalent to a theoretical plate derived by Van Deemter and his co-workers.

$$H.E.T.P. = 2\lambda d_p + \frac{2\gamma D_{gas}}{u} + \frac{8}{\pi^2} \frac{k'}{(1+k')^2} \frac{d_f^2}{D_{liq}} u$$

longitudinal	non-equilibrium
diffusion	effect
(eddy) (molecular)	

The graphical representation of this equation is shown in Fig. 8 (a modification by the writer of the usual presentation).

A study of the Van Deemter equation will yield an understanding of the actual processes taking place in a chromatographic column. The equation given above may be

Fig. 8. Graphical representation of the Rate equation in gas-liquid chromatography.

written for convenience:

$$\text{H.E.T.P.} = A + \frac{B}{u} + Cu \quad (v)$$

Predictions from Rate theory

(1) Carrier gas

(a) Flow rate

Equation (v) is that of a hyperbola. The minimum in the curve occurs at a value of $u = \sqrt{\frac{B}{C}}$ and $\text{H.E.T.P.} = A + 2\sqrt{BC}$.

Since at $u = \sqrt{\frac{B}{C}}$ height equivalent to a theoretical plate

is also a minimum, the column functions at the maximum efficiency. Since the flow rate is not constant throughout the column, because of the pressure drop from inlet to outlet, only a part of the column can operate at the maximum efficiency.

(b) Nature of carrier gas

The coefficient B in equation (v) contains the term D_{gas} which is the gas diffusivity. For maximum efficiency of operation therefore, (or minimum height equivalent to a theoretical plate), gases of low diffusivity should be used. Nitrogen and argon are preferable to hydrogen and helium from this point of view. However, due to the very high thermal conductivities of the latter two gases, they are often used with katharometer detection.

(c) Pressure of carrier gas

Diffusivity is proportional to the inverse of the gas pressure. High gas pressure will therefore yield higher efficiencies. The ratio of inlet to outlet pressures should be small in order that a large part of the column operates at a height equivalent to a theoretical plate corresponding to the optimum flow rate (Fig. 8).

2. Solid support

The factors influencing the solid support may be studied by considering the term A, the eddy diffusion term in equation (v). It would seem that higher efficiencies might be realized by decreasing the particle diameter. The parameter λ however, is characteristic of the uniformity of packing and its value decreases for larger particle diameters. λ also can be expected to decrease for a narrow range of spherical particles. Keulemans (1957) considers 30-50 or 50-80 mesh fire brick to be best for most applications.

3. Stationary liquid

The effect of the stationary liquid on the efficiency of the column appears in the resistance to mass transfer term in the Van Deemter equation

$$\frac{8}{\pi^2} \frac{k'}{(1+k')^2} \frac{d_f^2}{D_{liq}} u$$

The coefficient k' is the ratio of the amount of solute in the liquid to the amount of solute in the gas phase and is normally greater than one. Increasing k' will therefore decrease the height equivalent to a theoretical plate. Components with greater solubility in the liquid phase will thus increase the column efficiency. The term d_f , the effective film thickness, appears to the second power and a decrease in its size should increase the efficiency to a large extent. If, however, this is done by decreasing the amount of liquid, k' is also decreased and counteracts the increase in efficiency. With a porous support, decreasing the amount of stationary liquid beyond a certain limit leads only to an incomplete covering of the particles, which has a detrimental effect on the height equivalent to a theoretical plate. Usually, optimum conditions are achieved at 15% to 25% by weight of stationary liquid (Keulemans, 1957).

4. Dimensions and operating conditions of column

(a) Column length

The expression for the height equivalent to a theoretical plate is the ratio, column length divided by the number of theoretical plates, and is roughly equivalent to the reciprocal of column length. The efficiency increases with an increase in column length. The increase is not proportional to the increase of column length because an increased

pressure drop decreases the length of column operating under optimum conditions. According to Hausdorff and Brenner (1958), separation is approximately proportional to the square root of the column length.

(b) Column diameter

An increase in column diameter decreases the efficiency owing to increased broadening of bands. However, the capacity of the column is proportional to the square of the diameter.

(c) Sample size and mode of introduction

Because the assumptions made in the Rate theory are more fully realized at small solute concentrations the efficiency increases with decrease in sample size. The most efficient introduction of the sample owing to minimization of band tailing is in the form of a "plug". The concentration-time curve for the vapour arriving in the column is rectangular in this case.

(d) Temperature

Temperature affects the diffusivity in the liquid phase, D_{liq} , by changing the viscosity of the column liquid. In some cases the height equivalent to a theoretical plate may be lowered at increased temperatures but in other cases, adverse effects on k' and D_{gas} may increase height equivalent to a theoretical plate. DeWet and Pretorius (1958) obtained a relationship between temperature and height equivalent to

a theoretical plate in the form of a hyperbola

$$\text{H.E.T.P.} = \alpha + \beta T + \gamma T^{-1}$$

5. The nature of the stationary liquid

A solute is separated into its constituents owing to the difference in their partition coefficients. In principle, if the relative volatility of the constituents, which is the ratio of the partition coefficients, is greater than one, a separation can be effected.

The choice of solvent for a certain application is rather complicated and depends on many factors. The basic considerations are:

(i) The solvent should produce a differential partitioning of the components;

(ii) It should be non volatile at the temperature of the experiment;

(iii) It should have sufficient solvent power for the components.

The choice of solvent of high separating power for the solutes in question is governed by the forces of interaction between solute and solvent. These may be divided into four types:

- (i) Forces between permanent dipoles;
- (ii) Forces between a permanent and an induced dipole;
- (iii) Non-polar forces;
- (iv) Specific interaction forces.

Thus, with a non-polar solvent, non-polar solutes will be separated approximately according to their boiling points since the forces between solvent and solute will be similar to the forces between solute molecules. Polar solutes will elute from non-polar solvents more rapidly than non-polar solutes since the non-polar or dispersion forces will be absent. Similarly, polar solutes will be retarded to a greater extent by solvents with higher dipole moments.

CHAPTER III

APPARATUS, METHOD AND PRELIMINARY RESULTS

Introduction

The diagram of the apparatus used for the synthesis and purification of tetramethyllead by means of free methyl radicals is shown in Fig. 9. In order to describe clearly the design and construction of the whole apparatus, it has been divided into two main parts, which deal with:

(i) Production of free radicals and removal of the lead mirror to form tetramethyllead;

(ii) Gas chromatographic purification of the tetramethyllead.

Production of free radicals and mirror removal

The various methods available for the production of free radicals have been dealt with in Chapter II. In his studies on the feasibility of the synthesis of tetramethyllead by the action of free radicals on a lead mirror, Surkan (1956) experimented with the thermal and electrical discharge source. Various organic compounds such as acetone, methane and propane were used in this study. There were large amounts of

Fig. 9. Diagram of apparatus for the free radical synthesis of tetramethyllead.

contaminants in the same mass range as tetramethyllead and this prompted the present writer to experiment with other techniques. The photolysis of acetone was the first choice for a suitable free radical source.

Ultraviolet radiation was provided by a 150 watt mercury lamp. After the glass envelope was removed, the lamp was sealed inside a quartz tube. A lead mirror was deposited on the walls of this tube and cooled to room temperature. Acetone was passed through a needle valve at a pressure of 1/2 millimeter of mercury and was bombarded with ultraviolet radiation from the mercury lamp. No noticeable mirror removal took place although the experiment was continued for thirty minutes. The reaction products collected, amounting to about 5 ccs., were fractionally distilled to 1/2 cc. and further distillation was carried out under vacuum in the sample line of the mass spectrometer. Analysis of the sample in the mass spectrometer showed the presence of tetramethyllead, but the sensitivity was far short of that required for a satisfactory analysis.

An examination of the spectral energy distribution of various lamps shows that the lamp used produces 5 watts of power in the near ultraviolet. The most intense lamps manufactured produce 110 watts of radiation in this region and these produce radicals at a maximum rate of one hundredth of a mole per hour (Trotman-Dickenson, 1959). Assuming that

one percent of the radicals produced actually hit the mirror, the time required to remove 100 micrograms of lead would be approximately one minute. With the lamp used, this time would be increased by a factor of twenty.

There are many disadvantages associated with the use of lamps capable of high ultraviolet power. In the first place, efficient cooling is necessary and vacuum tight joints are required if the lamp is placed inside the reaction tube. Secondly, the commercially available lamps are inconveniently long; the General Electric HILS which gives 22 watts in the near ultraviolet is seven inches long. Finally, the time required to produce an amount of tetramethyllead sufficient for mass spectrometer analysis is the order of ten minutes and the amount of reaction products collected in that time presents problems with respect to the sample size requirements of gas chromatography.

Di-tertiary-butyl peroxide as a thermal source of free methyl radicals was suggested by Dr. G. B. Porter of the Department of Chemistry of this university. The details of this source have been dealt with in Chapter II. Preliminary experiments were performed in a slightly modified version of the apparatus shown in Fig. 2. At a temperature of 400° C, a mirror, previously deposited on the walls of the reaction tube, was removed in seconds. Mass spectrometer analysis of the reaction products confirmed the presence of tetramethyllead.

The successful experiment with a thermal source allowed the design and construction of the complete apparatus shown in Fig. 9.

The portion of the apparatus concerned with the free radical synthesis of tetramethyllead is composed of the following parts. The quartz reaction tube (a) is 19 inches long and 18 millimeters inside diameter. The fairly large dimension for the diameter was chosen to allow a high pumping speed and convenient manipulation of samples inside the tube. Di-tertiary-butyl peroxide is introduced into the heated region from a container (b) through a precision needle valve (c). The pressure of the peroxide is measured with a thermocouple gauge (d).

The incoming di-tertiary-butyl peroxide is decomposed with the aid of a furnace (e) which consists of a length of nichrome wire wound on an alundum core and insulated with asbestos tape. The temperature of the furnace, measured with a thermocouple is controlled with a variac. The sample may be introduced into the apparatus via an opening (f) in the reaction tube either in a boat and subsequently volatilized to form a mirror on the tube walls, or as a mirror deposited on a length of quartz tubing which fits inside the reaction tube.

The vacuum system consists of a mechanical backing pump

and a mercury diffusion pump which was made by Mr. J. Lees of the Department of Physics. This pump is capable of high speed, approximately twenty liters per second at optimum operating conditions. The pumping system is isolated from the reaction tube by means of a large bore stop cock (g) and liquid air trap (h) which prevents mercury vapours from diffusing into the liquid air trap (i) and contaminating the reaction products.

The rest of the apparatus which deals with the production of free radicals and mirror removal, consists of a hydrogen circulating system. Initially, this system was incorporated to reduce sulphides to the metal as a first step in the deposition of a mirror. However, owing to the large amounts of by-products involved, the reduction is carried out in a separate furnace and the hydrogen circulating system is used to clean the mirrors.

Spectroscopically pure hydrogen is introduced into the apparatus from a container (j) using a double stopcock arrangement and the pressure of the hydrogen is indicated by two mercury manometers. Circulation of the hydrogen is accomplished by means of an "inverted" mercury diffusion pump (k) designed and constructed by Mr. J. Lees. The principle of operation involved is the same as in an ordinary diffusion pump, except that mercury is forced upwards through a venturi nozzle. The circulating system may be isolated from the

reaction tube by means of stopcocks (1). An attempt was made throughout the apparatus to minimize the number of greased joints. The reason for this is twofold. First, tetramethyllead dissolves in grease with consequent contamination problems. The dissolved tetramethyllead is lost, and since the average amount produced for mass spectrometer analysis is in the order of 0.3 microliters, the loss might represent a substantial proportion of the sample. Secondly the writer feels that the large amounts of contaminants observed by Surkan (1956) were partially the result of radical reactions with stopcock grease. The greaseless stopcocks used in the present work are of two types. Stopcocks (1) are 1/8 inch Hoke bellows type valve. The disadvantage with this type is the need for glass to metal seals. The second type is an all glass stopcock with a Viton A seal. According to Doty and Ryason (1961) tetramethyllead is not adsorbed on Viton A and consequently this stopcock is used in the tetramethyllead collecting apparatus, described in the next section, where the chances of cross contamination are greatest.

Gas chromatographic purification of tetramethyllead

As a result of the reaction of free methyl radicals with a lead mirror, tetramethyllead together with the products of the pyrolysis of di-tertiary-butyl peroxide is trapped in trap (i). The next step is the separation by gas chromatography

of the tetramethyllead from the other reaction products. The separating line is shown in Fig. 9 and consists of the chromatographic column (m), katharometer (n) and a collecting assembly. Following an experiment, the sample contained in trap (i) is transferred to the top of the column and subsequently passed through with helium from a high pressure cylinder (o). The method of transferring the sample into the column was initially performed as shown in Fig. 10-1 (Bazinet and Walsh, 1960). The sample was transferred into the U-tube from trap (i) under vacuum by freezing in a liquid air trap. Helium was passed through the branch ~~1~~-4 and the sample was vapourized by placing the U-tube in a dewar containing water at 80° C. Manipulation of the 4-way stopcock allowed the helium to follow the path ~~1~~ - 2 - 3 - 4 and flush the vapourized sample into the column.

This method however, suffers from several disadvantages. In the first place, grease from the stopcock is washed down into the U-tube and requires constant, troublesome cleaning. The loss of tetramethyllead in the grease may be substantial in this case. Secondly, the method of sample introduction is far removed from the ideal plug, and consequently the bands of solute are distorted and the separation is rather poor.

The system presently used is illustrated in Fig. 10-2. The reaction products contained in trap (i) are transferred into a small bulb (p), previously joined to the apparatus.

Fig. 10. Techniques for introducing samples into a chromatographic column.

The bulbs are very conveniently made from 5 millimeter tubing by sealing one end in a hot flame and blowing out a centimeter diameter bubble. A thickened joint is made to facilitate removal of the bulb from the apparatus under vacuum.

The bubble containing the mixture to be separated is introduced into the top of the column which is then made gas tight with a serum cap. The bulb is crushed with a stainless steel ball. The shape of the eluted peaks obtained suggest that the mode of introduction approaches that of a plug. Likewise, the problem of grease contamination has been eliminated.

The column (m), shown in Fig. 9, consists of a 6.5 foot, 10 millimeter inside diameter helix of pyrex tubing. The length was chosen on the basis of experience gained by the writer in an earlier study (Ulrych, 1960) and preliminary experiments with a 4 foot column which had been used in that work. A uniform temperature of the column is maintained by a water bath. The packing used, 60-80 mesh ground firebrick obtained commercially, is prepared in the following manner. The correct amount of a suitable stationary liquid is dissolved in ether or ethanol and mixed with a suitable amount of firebrick. Details of the packing are considered elsewhere. The amount of solvent used should be such that the firebrick is just covered with liquid. This stage is quite

critical since it is necessary that the partitioning liquid be uniformly distributed and form a film around each support particle. When mixing is complete, the solvent is evaporated and the column is firmly packed. It is important to achieve uniform packing in order that the carrier gas distribute itself throughout the column and not produce channeling. Glass wool is used to plug the ends of the column.

There are various methods of analyzing the effluent, such as thermal conductivity bridge, vapour density balance, hydrogen flame and ionization detectors. Thermal conductivity, however, is the most widely used by virtue of its simplicity and is the method used by the writer. Fig. 11 shows the mechanical construction of the sensing instrument, commonly known as the katharometer, and the detector circuit.

The principle of the method is that heat is conducted away from a hot body, situated in a gas, at a rate depending on the nature of the gas, other factors being constant. The temperature of the tungsten sensing elements and hence their resistance is determined by the conductivity of the surrounding gas. Since absolute measurements using thermal conductivity are difficult, a differential technique was adopted by the writer, using two gas channels and two matched pairs of tungsten filaments. Pure carrier gas is passed through channel 1, through the column and then through channel 2. The difference in resistance of the heated wires due to the

Fig. 11. Details of thermal conductivity sensing device.

presence of volatile components in the effluent is measured by the Wheatstone bridge shown in Fig. 11. The bridge gives an out of balance voltage which is recorded on a suitable chart recorder. The particular mechanical arrangement shown in Fig. 11 was chosen to minimize effects of flow fluctuations at some expense of a fast response.

The sensitivity of the detector is controlled by two factors, the temperature of the sensing elements, and the relative change in thermal conductivity. Sensitivity increases for higher element temperatures, and this may be accomplished by increasing the bridge current. An upper limit is the stability of the base line which deteriorates considerably at high temperatures. The second factor depends on the type of carrier gas used. The requirements of a carrier gas which have been discussed in Chapter II are satisfied by a number of gases, the most readily available being hydrogen, helium, and nitrogen. The thermal conductivity of the above relative to air are 7.10, 5.53, and 0.996 respectively. Since the majority of organic components have thermal conductivities similar to nitrogen in value, the sensitivity of the katharometer is considerably greater with helium or hydrogen as the carrier gas. Owing to the hazards involved in the use of hydrogen, helium was chosen as the carrier gas.

The remaining part of the apparatus shown in Fig. 9 is used for the collection of tetramethyllead following gas

chromatographic separation. The collecting device consists of a dilute nitric acid bubbler (p), a liquid air trap (q) in which the desired portion of the column effluent is trapped, and a break seal tube (r) into which the sample contained in the trap (q) is transferred for mass spectrometer analysis. Vacuum is produced in the line with the aid of a backing pump. Stopcocks (s) and (t) are provided for isolating the system from the atmosphere and unwarranted constituents of the column effluent. Stopcock (t) is greaseless for the reasons previously discussed.

Design of a suitable chromatographic column

The products of the pyrolysis of di-tertiary-butyl peroxide are ethane, methane, acetone and higher boiling ketones. Since the pyrolysis is performed under fast flow conditions it is reasonable to assume that some of the di-tertiary-butyl peroxide will also be present in the reaction products.

The writer had at his disposal a 4 foot, 14 millimeter inside diameter column, which had been used in a previous study and had been designed to handle fairly large samples, of the order of 1/2 cc. The preliminary experiment with di-tertiary-butyl peroxide as a free radical source indicated that the amount of reaction products obtained would be smaller. As separations achieved are more efficient with a

narrower column owing to a decrease in band spreading, it was decided to make a new column of 10 millimeters inside diameter. The column length influences the separation obtained to a large extent. Some guidance as to the required length may be obtained from calculations performed on the 4 foot column and a consideration of Glueckauf's (1955) curves. Using the expression $n = \left(\frac{4d}{w}\right)^2$ (Appendix), and the elution curves for an average separation of tetramethyllead and ether in the 4 foot column, a value of 650 theoretical plates is obtained.

To determine the number of plates required for a particular band impurity (cf., Fig. 7) using Glueckauf's curves, one must know the relative volatility of the two components being separated. In this case the relative volatility of tetramethyllead and the highest boiling fraction is unknown. (The highest boiling fraction is taken here because the stationary liquid used separates roughly according to boiling point.) If however, an arbitrary value of 1.2 is assigned some idea of the column requirements may be obtained.

Assuming equal molar quantities of the two compounds (a most pessimistic estimate of the requirements), the number of plates required for a 0.01% band impurity is approximately 1700. Use of the 4 foot column would result in a 1% band impurity with the assumed relative volatility. Since the number of theoretical plates is proportional to the square root of the column length, the length of column required for a

0.01% band impurity is approximately $4 \times \sqrt{\frac{1700}{650}} = 6.5$ feet.

The dimensions of the column were thus chosen to be:
inside diameter, 10 millimeters; length, 6.5 feet.

The column packing used in the writer's previous study (Ulrych, 1960) consisted of commercially available 60-80 mesh, powdered fire brick with dinonyl phthalate as stationary liquid. Reasons for the choice of dinonyl phthalate were presented fully at the time, but briefly, it is a liquid of general applicability and separations are obtained roughly according to boiling point. The solid support proved very satisfactory and the first experiments were carried out with the 6.5 foot column packed with 25:100 parts by weight dinonyl phthalate on 60-80 mesh fire brick.

The first experiment performed was the separation of the products of the pyrolysis of di-tertiary-butyl peroxide under fast flow conditions. The technique adopted for the thermal decomposition, sample introduction into the column etc. is presented when the actual process used for the preparation of tetramethyllead is discussed.

The chromatogram for this experiment is reproduced in Fig. 12. (Corrections for base line drift have been applied in this figure.) The eluted peak appearing at the 18 minute mark was identified as di-tertiary-butyl peroxide by passing the undecomposed compound through the column. A di-tertiary-

Fig. 12. Separation of the reaction products of the pyrolysis of di-tertiary-butyl peroxide.

butyl peroxide peak is present because, owing to the fast flow requirement, a small proportion of the compound did not reach the dissociation temperature. Di-tertiary-butyl peroxide may be removed from the reaction products by raising the temperature of decomposition. This was not done in the preliminary experiments, however in order to allow the design of a column which would separate tetramethyllead from all the contaminants present.

The interpretation of the chromatogram shown in Fig. 12 is as follows:

- Peak (i) Methane;
(ii) Ethane;
(iii) Acetone and higher boiling ketones;
(iv) Di-tertiary-butyl peroxide.

The peaks are identified on the assumption that dinonyl phthalate separates components roughly according to boiling point. The resolution of peak (iii) into its components is illustrated in a subsequent chromatogram.

The next experiment performed was the separation of tetramethyllead and di-tertiary-butyl peroxide. Tetramethyllead was prepared using the standard Grignard reaction followed by fractional distillation (Ulrych, 1960). A few drops of di-tertiary-butyl peroxide were added and twenty microliters of the mixture were injected into the column which was

maintained at a temperature of 73° C. The carrier gas flow rate was adjusted to 150 millimeters per minute. The chromatogram obtained is shown in Fig. 13.

Calculations on the performance of the column gave the following results:

Number of theoretical plates using the tetramethyllead
peak = 1250;

Separation factor = 1.25.

Using Glueckauf's curves, the band impurity is approximately 0.01%. This figure assumes that the cut is made in such a way that the fractional impurity in both bands is equal, and therefore, to achieve the 0.01% value, the cut would have to be made close to the tetramethyllead peak with likelihood of loss. It was considered desirable, therefore, to increase the separation between the two components.

Such an increase may be attempted in two ways. The first is to alter either the temperature of the column, the carrier gas flow rate, the amount of stationary liquid, or a combination of all three. The second approach is to employ a stationary liquid of different properties. The writer adopted the latter approach.

The critical separation is between tetramethyllead and di-tertiary-butyl peroxide. The former is a non-polar liquid,

Fig. 13. Gas chromatographic separation of tetramethyllead. I.

Column: 6.5 ft. - 10 mm. I.D.
25:100 parts by weight of dinonyl
phthalate on 60:80 mesh fire brick.

Peak (i) Air
(ii) Ether
(iii) Di-tertiary-butyl
peroxide
(iv) Tetramethyllead

while the latter is polar. The stationary liquid used, dinonyl phthalate, is also polar and the solvent-solute reaction in the column may be described as follows:

Owing to the polarity of the solvent, interaction forces with di-tertiary-butyl peroxide are stronger. Consequently, retardation through the column is greater than it would be with a non-polar solvent. On the other hand, owing to its non-polar nature, tetramethyllead will be eluted more rapidly through a polar rather than through a non-polar solvent since the non-polar or dispersion forces between solute and solvent are less marked.

It follows from the above considerations that the use of a non-polar stationary liquid should improve the separation. With this in mind, the column was repacked using 25:100 parts by weight of type 2044 white paraffin oil.

Fig. 14 shows the chromatogram obtained for the separation of tetramethyllead from the products of the pyrolysis of di-tertiary-butyl peroxide using the new column. The separation has been improved substantially; the time interval between the leading edge of the di-tertiary-butyl peroxide peak and the tail of the tetramethyllead peak is more than two minutes. The fractional band impurity assuming equal molar quantities is given by the curves of Fig. 6 to be $10^{-6}\%$.

Fig. 14. Gas chromatographic separation of tetramethyllead. 2.

Fig. 14 shows the resolution of peak (iii) of Fig. 13 into three components, which are:

- Peak (iii) Acetone;
- (iv) Methyl ethyl ketone;
- (v) Higher boiling ketone.

The column properties are summarized in Table 4.

The separation of tetramethyllead with a calculated impurity of only $10^{-6}\%$ established the time necessary for the elution of tetramethyllead, with the stationary liquid used, at approximately 24 minutes.

In the analysis of Sudbury leads, the temperature of the decomposition of di-tertiary-butyl peroxide was raised from 450°C to 600°C to eliminate the compound from the reaction products. In order to diminish the amount of any tetramethyllead adsorbed on the solid support, a coarser grade of support and a shorter column were used. The properties and operating conditions of this column, column 2, are given in Table 4.

Under these operating conditions and with these column properties, the tetramethyllead was eluted after 24 minutes. This ensured that any di-tertiary-butyl peroxide, if it were present, was separated.

Table 4. Characteristics of chromatographic columns for the purification of tetramethyllead.

Column 1 Specifications

Carrier gas	Helium
Carrier gas flow rate	150 ml/min
Solid support	60-80 mesh fire brick
Stationary liquid	White paraffin oil, 25:100 pts. by wt.
Column dimensions	Length 6.5 ft., diameter 10 mm. I.D.
Detection	Katharometer
Column temperature	73°C

Performance as estimated from di-tertiary-butyl peroxide peak

Number of theoretical plates, $n = 1540$
Height equivalent to a theoretical plate = 1.3 mm.
Retention volume $V_R = 2720$ cc.

Performance as estimated from tetramethyllead peak

Number of theoretical plates, $n = 1560$
Height equivalent to a theoretical plate = 1.3 mm.
Retention volume $V_R = 3560$ cc.
Relative volatility (ratio of partition coefficients) $\alpha = 1.31$
Fractional band impurity (from Fig. 6) = 10^{-8}

Column 2 Specifications

Carrier gas	Helium
Carrier gas flow rate	100 ml/min
Solid support	40-60 mesh fire brick
Stationary liquid	White paraffin oil 33:100 pts. by wt.
Column dimensions	Length 5 ft., diameter 10 mm. I.D.
Detection	Katharometer
Column temperature	65°C

Performance as estimated from tetramethyllead peak

Number of theoretical plates, $n = 1100$
Height equivalent to a theoretical plate = 1.4 mm.
Retention volume $V_R = 2400$ cc.

The preparation of lead mirrors from various sulphides

A lead mirror may be introduced into the apparatus in one of two ways. The first method is to place lead in a ceramic combustion boat inside the reaction tube and heat to volatilize the lead to form a mirror on the walls of the tube. The second method is to deposit a lead mirror on a length of quartz tubing by some suitable means and place it in the reaction tube.

Preliminary experiments were carried out using the first of the two techniques, but since free lead is not found in geological formations, a means of producing a lead mirror from lead minerals or from substances containing lead as a minor constituent was necessary.

Preliminary experiments were performed using reagent lead sulphide. It was found that conversion of lead sulphide to lead and hydrogen sulphide was not possible using the hydrogen circulating system previously described since the permissible pressure of hydrogen for efficient pump operation, 1 to 2 centimeters, was too low to convert the lead sulphide before sublimation. Conversion of lead sulphide to free lead was accomplished in two ways. The first method used a hydrogen furnace shown in Fig. 15 at a temperature of 900°C. The lead was obtained in the form of a mirror on the cooler portions of the tube. The second method employed nitrogen

Fig. 15. Diagram of resistance furnace.

as a carrier gas and careful heating with an oxygen-gas torch. The amount of heat applied was found to be quite critical. If too much was applied suddenly, the whole sample sublimed as a lead sulphide mirror on the tube walls. With the correct amount of heat small lead globules remained in the boat.

The first attempts to produce a lead mirror from a galena sample were carried out in an atmosphere of nitrogen. One milligram of galena was carefully crushed, placed in a boat and the procedure used with reagent lead sulphide was repeated. This experiment was unsuccessful as the galena always sublimed as a lead sulphide mirror. The difference in behaviour was attributed to the different state of the reagent lead which is extremely fine grained, while the crushed galena is comprised of much larger crystals. Diffusion of sulphur against the flow occurs, and any free lead formed reacts with the sulphur to form lead sulphide. An attempt was made to convert a single galena crystal, situated at the very end of the tube, to lead by heating it in a flow of nitrogen. Free lead was obtained but extremely careful heating was required. Too much heat volatilized the sample, - too little did not break the lead-sulphur bond. It was found necessary to apply heat intermittently to allow the nitrogen time to drive all the sulphur fumes from the tube and not allow the reverse reaction to take place. Gallo and Del Guerra (1951) quote 440°C . as the initial desulphurization

temperature and 600°C. as the conversion temperature of the sulphide to metal.

Conversion of galena to free lead in the hydrogen furnace presented no problem, the lead being obtained as a mirror on the walls of the quartz tube.

The exact manner of occurrence of lead in pyrite and pyrrhotite is unknown. The various possibilities are presented in Chapter IV. A semiquantitative spectrographic analysis of a pyrite and pyrrhotite sample suggested a lead content in the neighbourhood of 2000 p.p.m. for the pyrite and 200 p.p.m. for the pyrrhotite.

Half a gram of the pyrite, crushed to less than 100 mesh, was contained in a combustion boat placed in a quartz tube and inserted into the hydrogen furnace of Fig. 15 at a temperature of 1000°C. When sulphur fumes were no longer given off, the tube was moved to a cool portion of the furnace and any mirror on the tube walls was allowed to cool in a hydrogen atmosphere to prevent oxidation. Sulphur which had sublimed was driven off by reversing the tube in the furnace. At the same time, the metallic mirror moved through the heated zone to the cool part of the tube. This procedure was repeated until no more hydrogen sulphide fumes were noted. The quartz tube containing the mirror was then placed inside the reaction

tube of the apparatus shown in Fig. 9.

An attempt to remove the mirror by the action of free methyl radicals produced a negative result. An analysis of the composition of the mirror, carried out by Dr. R. E. Delavault of the Department of Geology, showed that the mirror was mainly composed of lead, but was contaminated to some degree by iron. The existence of the iron contaminant is hard to understand since the mirror was moved the length of the tube several times. A further experiment at a reduced temperature of 900°C produced a similar result and only a small part of the mirror was removed, the removal being very slow. The contamination problem was solved using the hydrogen circulating system. The tubular furnace (e) in Fig. 9 was moved over the inserted mirror and the temperature raised to 600°C. Hydrogen was introduced at a pressure of 1 centimeter and circulated with the aid of the "venturi" pump. This procedure accomplished a distillation of the lead mirror at reduced pressure. The larger fraction of the mirror moved through the heated zone whereas a black residue remained in the original mirror position. The former mirror fraction was easily removed by free methyl radicals.

A similar procedure was carried out using 3 grams of pyrrhotite. The temperature of the hydrogen furnace was maintained at 900°C. Following the distillation described above only a slightly visible deposit remained on the quartz tube.

Procedure for the synthesis of tetramethyllead

A lead mirror deposited on the inside of a quartz tube, 19 inches in length and 18 millimeters in inside diameter, is inserted into the apparatus through an opening (f), Fig. 9. Any oxides or other contaminants present on the mirror are removed at 600°C in a flow of hydrogen from the container (j) and circulated by means of the "venturi" pump (k). A stop-cock (g) isolates the system from the pumps.

Furnace (e), at the desired temperature, is moved to within two centimeters of the leading edge of the mirror, which is cooled to room temperature by means of a small blower motor. Di-tertiary-butyl peroxide is admitted through the needle valve (c) at a pressure approximately equal to 0.2 millimeters of mercury. Following the complete removal of the lead mirror, which usually takes less than one minute, the furnace is allowed to cool below the decomposition temperature of tetramethyllead, 120°C, and the reaction products contained in trap (i) are transferred into the bubble container (p).

The container (p) is removed from the apparatus and inserted into the chromatographic column in the manner illustrated in Fig. 10-2. A stainless steel ball is raised by a magnet in the connecting arm and released to crush the bubble container, permitting the sample to be flushed through

the column by the carrier gas. The separations are monitored on a chart recorder. The unwanted constituents of the effluent are allowed to bubble away, whereas the tetramethyllead is trapped in trap (q) and transferred into a break-seal tube.

Preliminary results

Twelve samples of tetramethyllead were prepared using the free radical technique and analyzed in a mass spectrometer. The experiments, using metallic lead and various sulphide-minerals, were designed to determine the best conditions for mirror formation, mirror removal and gas chromatographic separation. In experiments with metallic lead, the sample was volatilized on to the walls of the reaction tube. In the case of sulphides, a lead mirror was either deposited on the inside of a quartz tube, or the sulphide was converted to metallic lead and volatilized. Of the twelve samples, six were prepared from 500 microgram quantities of metallic lead, two from reagent lead sulphide, two from galena and one each from pyrite and pyrrhotite.

The sensitivity of mass spectrometer analysis of tetramethyllead prepared from approximately 500 micrograms of lead using the free radical technique was comparable to that obtained from 100 milligrams of lead using the Grignard synthesis. The precision of the results was typically about

0.3%. Following the preliminary analyses, however, the sensitivity of the mass spectrometer was increased by a factor of three and the precision of measurement improved.

A comparison of two typical analyses, prepared using the free radical technique and the Grignard synthesis is shown in Table 5. It may be concluded that equally high precision of measurement can be obtained from approximately 500 micrograms of lead. A sample of a trimethyl spectrum obtained in the analysis of leads from the Sudbury district (Chapter IV) is shown in Fig. 16.

It is necessary to consider the various ways in which contamination might occur. Consideration of the technique suggest the following:

The first step in the synthesis of tetramethyllead is the volatilization of a lead mirror. The contamination here is minimized by cleaning the tube which is to contain the mirror, and the quartz tube of the resistance furnace with nitric acid.

A source of contamination was brought to light during the analysis of lead from a pyrrhotite. The ratio of mass 254/mass 253 which is used to correct for C_{13} was found to be 0.034, whereas over the course of this project this ratio has been 0.0310 ± 0.0002 . The increased abundance of mass 254

Table 5. Typical precision of analyses with the free radical and Grignard techniques for synthesis of tetramethyllead.

Free radical technique

U.B.C. No. 359 Sudbury, Ontario

No. of pairs = 6

Mass No.	249	250	251	252	253	254
Abundance %	1.4256	.2256	22.3345	23.0092	51.4266	1.5784
Std. Dev.	.0012	.0013	.0070	.0063	.0092	.0042

Grignard technique

U.B.C. No. 165 Captain's Flat, Australia

Analyzed by R.G. Ostic

No. of pairs = 5

Mass No.	249	250	251	252	253	254
Abundance %	1.3038	.2364	23.9343	21.7690	51.1122	1.6444
Std. Dev.	.0012	.0019	.0023	.0061	.0074	.0014

Fig. 16. Trimethyllead spectrum obtained using the free radical technique.

was attributed to bismuth trimethyl. Bismuth trimethyl has the same boiling point as tetramethyllead and would not be separated in the chromatographic process.

Since the ratio mass 254/mass 253 is constant to one per cent, however, the presence of bismuth in the sample can be identified and a suitable correction applied.

A further possibility of contamination arises from memory effects in the reaction tube. To counteract this, the lead mirror is deposited on the inside of a quartz tube equal in length to the reaction tube. The whole process, which consists of the distillation of the mirror and the synthesis of tetramethyllead occurs in this tube. Since the tube is 19 inches long, the likelihood of lead being deposited outside the quartz tube is extremely small. The extent of contamination in this portion of the apparatus may be evaluated from the analysis of a galena sample discussed below.

The final source of contamination is the possibility of isotopic exchange between a particular sample of tetramethyllead and any tetramethyllead remaining on the solid support of the chromatographic column from previous analyses. The obvious way to eliminate this possibility is to change the column packing. In order to estimate the amount of contamination possible, the column packing was not changed in the course of the preliminary experiments.

The analyses of the samples prepared in the preliminary experiments are given in Table 6.

The large discrepancy in the actual and observed ratios of sample 3 is very probably due to contamination with lead which had not been removed in the previous experiment.

Mass spectrometer analyses for samples 4, 5 and 6 are not available. Loss of tetramethyllead occurred during pumping at dry ice temperature. This procedure was tried in an attempt to eliminate the volatile products of the decomposition of di-tertiary-butyl peroxide prior to chromatographic separation.

The crystal of galena used in sample 9 was converted to metallic lead in nitrogen. Due to poor mirror removal by free radicals insufficient tetramethyllead was formed for an adequate analysis.

Samples 11 and 12, from the Kootenay Arc in British Columbia were supplied by Mr. A. J. Sinclair of the Department of Geology. The pyrite, sample 11, contained approximately 2000 p.p.m. of lead. The lead content of the pyrrhotite was approximately 200 p.p.m.

The observed and actual lead isotope ratios for sample 10 differ by 1%. If the isotopic abundances of the contaminating lead are assumed to be that of sample 8, the amount of

Table 6. Lead isotope abundances and description of samples used in preliminary experiments

Sample No. and description	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
1 } 500 μ g reagent lead	20.92	15.96	37.17
2 } 500 μ g reagent lead	21.12	16.00	37.93
3 500 μ g radiogenic lead	293.3	37.62	38.40
3 Actual values	1471	146.3	48.67
4 } 500 μ g reagent lead	-	-	-
5 } 500 μ g reagent lead	-	-	-
6 } 500 μ g reagent lead	-	-	-
7 } 1 mg reagent PbS	20.67	15.87	38.50
8 } 1 mg reagent PbS	20.58	15.82	38.42
9 Galena crystal	-	-	-
10 1 mg galena	16.27	15.59	36.14
*10 Actual values	16.11	15.53	35.96
11 1/2 gm pyrite	19.17	15.84	39.64
12 3 gm pyrrhotite	21.50	15.84	38.70

* UBC No. 34 (Kollar, Russell and Ulrych, 1960)

contamination present is 3.5%. Part of this contamination is undoubtedly due to the reaction of methyl radicals with lead deposited on the walls of the reaction tube in experiments with metallic lead. This source is completely absent in actual preparations. Furthermore, the usual procedure of flushing the column with ether at 80°C, a number of times was not used.

A possible 3.5% contamination in the free radical technique from all causes is an extremely pessimistic estimate, since no precautions were taken.

This conclusion is certainly borne out by the results of the analyses of sample No. 359 (Table 8, Chapter IV) which agree to within 0.2%. This sample was prepared twice. The first preparation preceded while the second one followed the preparation of the samples with anomalous lead isotope abundances. Furthermore, the tetramethyllead synthesized in the second preparation was separated chromatographically following the separation of samples No. 361 and No. 362 without changing the column packing.

CHAPTER IV

LEAD ISOTOPE ABUNDANCES FROM SUDBURY, ONTARIO

Introduction

The first application of the free radical technique has been to study lead isotope abundances of samples from Sudbury, Ontario. The mining district at Sudbury has been, for many years, one of the world's largest nickel producing areas. It was one of the first areas from which lead isotope abundances were available. These were published in 1954. (Russell et al., 1954). The analyses constituted the first interpretation of a suite of anomalous leads whose Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} isotope ratios were considered to be linearly related. Since then, other examples of this type of linear relationship have been discovered (Farquhar and Russell, 1957; Russell, Ulrych and Kollar, 1961). The interpretation proposed by Russell et al. (1954) has been further developed by Farquhar and Russell (1957) and Kanasewich (in press) into a powerful geochronological tool.

The age relationships in the Sudbury district have been the object of intensive study. At least 54 potassium-argon and rubidium-strontium ages are available representing most of the geological formations in the area. (Fairbairn,

Hurley and Pinson, 1960; Davis et al, 1957; Wetherill, Davis and Tilton, 1960). However, these have not been sufficient to determine the sequence of events which have affected the area.

In view of the ambiguity of the results obtained from the many analyses using conventional dating methods, the writer thought it reasonable to go back to the older approach of Russell et al.(1954) to try to obtain additional information about this important and interesting area.

The area for which isotopic data is available represents over 1000 square miles; the predominant feature is a basin-shaped structure approximately 40 miles long and 20 miles wide. The major axis of the basin strikes ENE and is parallel to the Grenville front. Fig. 17 is a generalized map of the district and shows the relevant features which may be identified as follows (Thomson, 1956):

The most significant structure is the nickel irruptive which completely circumscribes the basin. The northern boundary of this formation dips south at 30 to 50 degrees whereas the southern boundary is nearly vertical. The nickel irruptive is composed of norite and quartz diorite along the outer edge and granophyre (locally referred to as micropegmatite) on the inner edge. The boundary between the norite and micropegmatite is transitional.

LEGEND

PRECAMBRIAN

Killarnean metamorphic complex
Granophyre (micropegmatite)	} Nickel irruptive
Norite and quartz diorite
Gabbro, amphibolite
Cobalt sedimentary group
Bruce sedimentary group
Granitic intrusives
Copper Cliff rhyolite
Sedimentary group	
	Inside Basin: Onwatin-Chelmsford formation	
	Argillite, slate, arkose and greywacke	
	Outside Basin: McKim-Mississagi formation	
	Quartzite, greywacke and conglomerate
Volcanic group	
	Inside Basin: Onaping formation	
	Andesitic tuff, coarse tuff-breccia and lapilli tuff (glowing avalanche deposits)	
	Outside Basin: Stobie formation	
	Lavas, sediments, rhyolitic intrusions and glowing avalanche deposits	

SYMBOLS

U Radioactive quartz-pebble conglomerate

Major fault

Mine

1. Anthraxolite pit	5. Garson	8. McKim
2. Errington	6. Stobie	9. Creighton
3. Hardy	7. Frood	10. Worthington
4. Falconbridge		

Fig. 17 (cont'd.)

The Precambrian is represented both inside and outside the basin by a sedimentary and a volcanic group. Inside the irruptive the volcanic group is referred to as the Onaping formation and consists of coarse tuffaceous breccia and lapilli tuff. The sedimentary group, the Onwatin formation, consists of argillite, greywacke and slate. The volcanic and sedimentary groups outside the irruptive are known as the Stobie and McKim-Mississagi formations respectively. These are cut by intrusions of various ages which occur all around the irruptive.

The first lead isotope analyses reported from Sudbury were obtained by Russell et al. (1954) from a suite of galenas. These results, including two additional ones (Russell and Farquhar, 1960), are presented in Fig. 18 as a plot of Pb^{206}/Pb^{204} against Pb^{207}/Pb^{204} . It can be seen that the leads fall roughly into two groups. The one group contains less radiogenic lead, whereas the other group contains considerably more. The leads in the latter group are classified anomalous because their isotope ratios could not have been formed in a single closed uranium-thorium-lead system.

On the basis of the linear relationships shown in Fig. 18, Russell et al. (1954) postulated that the anomalous leads were "a series of mixtures of a single ordinary lead and a single radiogenic lead in varying proportions". This assumption implies a two-event history for the leads. The

Fig. 18. Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads:
University of Toronto analyses.

above authors calculated a limit to the time of separation of the leads from their primary source. This was found by solving the limiting case for which the two events coincide.

Farquhar and Russell (1957) extended the interpretation of the linear relationship to include the limiting age for the source of the radiogenic component.

The two-limiting ages for the Sudbury district, as calculated by Russell and Farquhar (1960), are as follows:

Maximum age of the source of the system from which the component was derived = 2200 ± 100 million years.

Maximum time of emplacement of the anomalous galenas = 1340 ± 60 million years.

Experimental results

The samples which have been analyzed in this study were obtained from the Department of Geology, University of Western Ontario and from A. J. Naldrett of the Department of Geology, Queen's University. The samples are described in Table 7.

The eight samples analyzed included four pyrites and one marcasite. The minor elements may be housed in the sulphide in a number of ways. According to Auger (1941) these are admixed solid inclusions, fluid inclusions, exsolution

Table 7. Location and geological description of
samples from Sudbury, Ontario

Sample No.	Description of Sample
335	Falconbridge mine. "Primary" marcasite with calcite from vein. 2975 foot level. West of mine shaft.
338	Hardy mine. "Reaction" pyrite occurring as euhedral grains around larger pyrrhotite grains (Naldrett private communication).
339	Hardy mine. Late supergene pyrite occurring as small cubes scattered throughout the ore near fault zones or as larger masses within the gouge of the faults themselves (Naldrett private communication).
358	Errington mine. Massive ore sulphides. An example of coarser than usual mineralization.
359	Errington mine. High sulphide ore from a diamond-drill core.
361	Errington mine. Massive patch pyrite in Onwatin slate. 1.5 feet from argillite contact.
362	Balfour Twp. 1 1/4 miles south of Larchwood corner. Coarse cubic pyrite from anthraxolite pit or vicinity. Possibly in contact with anthraxolite-quartz-pyrite vein.

products and solid solutions. The latter may be subdivided into substitutional, interstitial and "omission" types of solid solution. Auger's study of the minor elements in pyrite suggest that lead is not contained in the form of inclusions. The conclusion was reached on the basis of the constancy of spectrographic results on portions of the same sample of carefully selected pyrite crystals. The small average concentration of lead in sulphides, of the order of 200 p.p.m., tends to rule out exsolution as the mode of occurrence. The possibility of the lead existing in the form of solid solution may be examined in the light of the available rules governing atomic substitution. However, as pointed out by Ahrens (1953), care must be taken in applying these rules to sulphides owing to their predominantly covalent nature and the ability of sulphide precipitates to co-precipitate and occlude a variety of elements. The large difference in ionic radius, however, between lead ($1.2 \text{ \AA}$) and iron ($0.74 \text{ \AA}$) and the highly electronegative* nature of lead ions (1.6) would tend to prohibit any atomic substitution in a sulphide lattice. This probably also applies to omission solid solution associated with defect lattices, since such a lattice would have to be considerably stretched to accommodate a lead ion.

* See, for example, A.E. Ringwood, *Geochim. et Cosmochim. Acta* 7, 189 (1955).

It would seem therefore, that the lead is contained as an interstitial solid solution in which the lead ions fit into interstices in the sulphide lattice. Since Auger's (1941) analyses were carried out on specially selected sulphide crystals, it is probable that in an average sulphide sample, trace lead is contained both as an interstitial solution and as minute galena inclusions.

Information concerning the amount of lead in pyrites is rather scant. Fleischer (1955) reports the results of the analyses of 24 samples. Hawley and Nichol (1961) give the lead content of pyrites in magmatic nickel and hydrothermal copper and gold ores. In the latter paper the average concentration of lead in 5 pyrites from the district of Sudbury was found to be 170 p.p.m.

An approximate estimate of the lead content in the samples which have been analyzed during the present research may be obtained from the chromatograms, since the area of the eluted tetramethyllead peak is proportional to the amount present. Sample No. 1 was prepared from 1.5 milligrams of galena. The values for the lead content which are given in Table 8 have been calculated on the assumption of a 100% efficiency in the synthesis of tetramethyllead and should be considered semi-quantitative.

In the course of the preparation of the Sudbury samples,

Table 8. Isotopic analyses of Sudbury leads
University of British Columbia analyses*

Sample No.	Approximate lead content p.p.m.	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴	Th ²³² /U ²³⁸ for 2nd stage (referred to present)
1 Standard**		16.116	15.542	36.068	
1 Measured***		16.064	15.466	35.941	
359		15.614	15.469	35.755	
359		15.587	15.442	35.737	
358		16.011	15.542	35.989	2.36 ± .67
361	90	16.279	15.582	36.055	1.75 ± .44
362	120	17.861	15.777	35.973	0.39 ± .21
338	250	18.821	15.856	42.660	7.18 ± .20
339	100	20.732	16.126	43.281	5.14 ± .09
335	500	23.607	16.536	44.806	3.98 ± .05

* Isotope ratios are normalized to Broken Hill standard No. 1

** Kollar, Russell and Ulrych (1960)

*** Mean of two analyses

Table 8. (cont'd)
University of Toronto analyses*

Sample No.	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
232	15.756	15.585	36.080
518	16.022	15.440	35.638
309	16.194	15.695	36.442
312	22.575	16.415	44.296
234	22.688	16.368	44.213
217	22.764	16.503	44.270
311	22.699	16.389	44.608
303	23.136	16.492	44.645
305	23.343	16.633	44.725
211	25.817	16.706	51.825

* Isotope ratios given by Russell and Farquhar (1960) have been corrected for tailing.

the chromatographic column packing was changed three times. The column was first repacked following the separation of samples No. 359, 361, 362 and 359. The second change followed the separation of Nos. 339, 338 and 335. The column was repacked again following the separation of No. 358, in order to purify sample No. 1.

Mass spectrometer analyses were carried out using a 12 inch, 90 degree sector instrument with a modified Nier-type gas source. The mass spectrometer is described in detail by Kollar (1960). The lead isotope abundances for the samples which have been analyzed are presented in Table 8. Following the usual practice at this laboratory, the results have been normalized to the isotopic abundances of No. 1 determined by Kollar, Russell and Ulrych (1960).

The experimental results are plotted in Figs. 19 and 20. In order to compare these results with those of the earlier studies, University of Toronto analyses have been included in these figures and in Table 8. The ten Toronto values which are shown have been recalculated to include a correction for the effects of tailing of the peaks due to scattering of ions in the analyzer tube (Russell and Slawson, 1962). These corrections, which are approximately proportional to the pressure in the tube, were calculated from the actual spectrograms made available by Dr. R. M. Farquhar of the University of Toronto. The effect of the tailing

Fig. 19. Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads. University of British Columbia and University of Toronto analyses.

Fig. 20. Pb^{208}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Sudbury leads. University of British Columbia and University of Toronto analyses.

correction on the 10 Toronto analyses has been twofold. Firstly, the slope of the straight line relating $\text{Pb}^{206}/\text{Pb}^{204}$ to $\text{Pb}^{207}/\text{Pb}^{204}$ was changed from 0.130 ± 0.008 to 0.125 ± 0.007 . Secondly, the line was displaced downwards by about 0.6% of the average $\text{Pb}^{207}/\text{Pb}^{204}$ value.

The significant features of the new analyses are the considerable reduction of scatter about a single straight line and the distribution of points along the line, in contrast to the Toronto values which were concentrated about two points. In the opinion of the writer, these new data provide the first convincing evidence that the leads from Sudbury may form a simple anomalous suite of the type postulated by Russell et al. (1954). The interpretations which are presented in this study are based on the assumption that the linear relationship between $\text{Pb}^{206}/\text{Pb}^{204}$ and $\text{Pb}^{207}/\text{Pb}^{204}$ is due to a series of mixtures of a common and a radiogenic* lead. However, it is necessary to consider also other possible processes which would yield a similar relationship.

Another plausible process has recently been suggested by Russell, Kanasewich and Ozard (in press). These authors calculated the lead isotope abundances for hypothetical leads which were assumed to have developed in a succession of closed systems. The isotope ratios $\text{Pb}^{206}/\text{Pb}^{204}$ and $\text{Pb}^{207}/\text{Pb}^{204}$

* which is mathematically equivalent to a two-stage growth process of the type discussed by Kanasewich (1962)

followed a linear trend, but a lateral spread was present. For the results which have been obtained in this study, the points lie off the best straight line defined by them by amounts which are equivalent to a standard deviation of 0.37% in the $\text{Pb}^{207}/\text{Pb}^{204}$ ratio. The calculations by Russell, Kanasewich and Ozard for the "frequently-mixed" model suggest that the deviation would be greater than 0.7% if the samples corresponded to a three-stage model in which the final two stages were of comparable importance in altering the isotope ratios. Since the lateral spread becomes proportionately larger as the number of stages is increased, it may be concluded from the very small spread that the history of the leads can be explained by a comparatively simple model.

Other interpretations are possible. For example, one cannot exclude the possibility that two or three of the least radiogenic samples are in fact ordinary leads of different ages. Moreover, any group of lead isotope analyses, even if linearly related on a $\text{Pb}^{207}/\text{Pb}^{204}$ vs. $\text{Pb}^{206}/\text{Pb}^{204}$ plot, can be explained by an infinite number of models providing that there is no restriction on the number of separate stages involved in their evolution. The interpretations which follow are those which require the minimum number of separate events. This restriction is implicit in most lead isotope interpretations.

Interpretations of the Sudbury lead isotope ratios

Lead isotope interpretations are based on the four stable isotopes of mass 204, 206, 207 and 208. The latter three are identical with the end products of the uranium-238, uranium-235 and thorium-232 decay chains.

The development of a particular lead from primeval ratios a_0 , b_0 and c_0 between the initial time t_0 and a final time t can be represented by one of the integral equations:

$$\begin{aligned} x &= a_0 + \int_t^{t_0} \alpha V(t) e^{\lambda t} d(\lambda t) \\ y &= b_0 + \int_t^{t_0} V(t) e^{\lambda' t} d(\lambda' t) \\ z &= c_0 + \int_t^{t_0} W(t) e^{\lambda'' t} d(\lambda'' t) \end{aligned} \tag{1}$$

The symbols used in these equations are defined in Table 9.

The equations above may be replaced by summations if it is assumed that V and W are constants over discrete intervals of time (Russell, Kanasewich and Ozard, in press).

Table 9. Definition of symbols used in the calculation of the ages of the Sudbury leads.

Isotope Ratio	At present $t = 0$	At time t	At time t_0
$\frac{\text{Pb}^{206}}{\text{Pb}^{204}}$	a	x	a_0
$\frac{\text{Pb}^{207}}{\text{Pb}^{204}}$	b	y	b_0
$\frac{\text{Pb}^{208}}{\text{Pb}^{204}}$	c	z	c_0
$\frac{\text{U}^{238}}{\text{Pb}^{204}}$	$137.8V_0^*$	$137.8V_0e^{\lambda t}$	$137.8V_0e^{\lambda t_0}$
$\frac{\text{U}^{235}}{\text{Pb}^{204}}$	V_0	$V_0e^{\lambda' t}$	$V_0e^{\lambda' t_0}$
$\frac{\text{Th}^{232}}{\text{Pb}^{204}}$	W_0	$W_0e^{\lambda'' t}$	$W_0e^{\lambda'' t_0}$
Decay Constants	Value in $10^{-9}(\text{years})^{-1}$		Parent Atom
λ	0.1537**		U^{238}
λ'	0.9722		U^{235}
λ''	0.0499		Th^{232}

* $\alpha = \text{U}^{238} : \text{U}^{235} = 137.8 : 1$ (Inghram, 1947)

** Kovarik, A.F. and Adams, N.E., Jr. Phys. Rev. 98, 46, 1955.

Fleming, E.H., Jr., Ghiorso, A. and Cunningham, B.B.
Phys. Rev. 88, 642, 1952.

Picciotto, E. and Wilgain, S. Nuovo Cim. Ser. 10,
4, 1525, 1956.

$$\begin{aligned}
 x &= a_0 + \alpha \sum_{i=0}^{i=m-1} V_i (e^{\lambda t_i} - e^{\lambda t_{i+1}}) \\
 y &= b_0 + \sum_{i=0}^{i=m-1} V_i (e^{\lambda' t_i} - e^{\lambda' t_{i+1}}) \\
 z &= c_0 + \sum_{i=0}^{i=m-1} W_i (e^{\lambda'' t_i} - e^{\lambda'' t_{i+1}})
 \end{aligned} \tag{2}$$

Limiting values to the age of the source of the radio-genic component and time of emplacement of the anomalous leads can be calculated with the method of Russell et al. (1954) and Farquhar and Russell (1957).

In this it is assumed that $m = 2$ in the summation equations and, if the slope of the straight line is R ,

$$R = \frac{e^{\lambda' t_1} - e^{\lambda' t_2}}{\alpha (e^{\lambda t_1} - e^{\lambda t_2})} \tag{3}$$

Limiting times occur for $t_2 = 0$ and for $t_1 = t_2$.

In the first case the anomalous leads are assumed to have been deposited recently. In the second case, it is supposed that the lead isotopes were generated in a time short compared to the half-life of uranium-235.

For the Sudbury district, using the results of this study, these limiting times are calculated as follows:

Slope of the line = $R = 0.131 \pm 0.003$

Maximum age of the source of the radiogenic component = 2150 ± 50 million years

Oldest possible time of final emplacement of the anomalous leads = 1280 ± 50 million years

The term "final emplacement" is here used in the sense that significant chemical alteration occurred at least this recently.

Since the interpretations of Russell and Farquhar were carried out, Kanasewich (1962 and in press) has restated and extended the interpretation of anomalous leads. In particular, he has considered the quantitative interpretation of the general two-stage model, and a particular three-stage model. Both of these interpretations will be considered in relation to the observed abundances for the Sudbury basin.

The physical basis for the two-stage model has been stated by Kanasewich as follows. Time t_1 is assumed to be the time of deposition of an ordinary lead. Contemporaneously, uranium and thorium were introduced into the

lead environment. At time t_2 tectonic activity occurred, and the ordinary lead was mixed with radiogenic lead which formed between time t_1 and t_2 . The mixing need not be episodic but could occur continuously if part of the lead was mixed into the uranium environment at t_1 and was later extracted.

The event t_1 , which corresponds to the age of the ordinary lead, can be easily evaluated if the isotope ratios are known; since the ordinary leads are by definition the product of a single growth stage $m = 1$ and equations (1) become

$$\begin{aligned} x &= a_0 + \alpha V_0 (e^{\lambda t_0} - e^{\lambda t_1}) \\ y &= b_0 + V_0 (e^{\lambda' t_0} - e^{\lambda' t_1}) \\ z &= c_0 + W_0 (e^{\lambda'' t_0} - e^{\lambda'' t_1}) \end{aligned} \tag{4}$$

If three ratios x , y , z are known, three unknowns t_1 , V_0 and W_0 can be determined. The values of the parameters V_0 and W_0 provide a check on the assumption of a single stage growth process since these parameters are observed to be very similar for all ordinary leads which have been studied in detail.

The values for the constants a_0 , b_0 , c_0 and t_0 have recently been recalculated by Murthy and Patterson (1962) from meteoritic data. They are $a_0 = 9.56$, $b_0 = 10.42$, $c_0 = 29.71$ and $t_0 = 4.55 \times 10^9$ years.

The question arises as to whether the least radiogenic sample studied, No. 359 (Fig. 19) is in fact the ordinary lead of age t_1 , or whether it is an anomalous lead. The values of V_0 and W_0 calculated for this sample on the basis of a single stage model are compared in Table 10 with the corresponding values for other samples which have been analyzed at this laboratory and which are believed to be ordinary. The values for these parameters appear to be slightly higher than for the other samples in the table. However any sample lying further to the left on the same anomalous straight line would give even higher apparent values for V_0 and W_0 . Therefore it is likely that this sample defines a point which is at least close to the starting point of the line. Whether or not this starting point is actually an ordinary lead might be determined by doing careful intercomparisons of the isotope ratios of other samples from the same mine. However, this was not included in the present project. It is considered that the assumption that No. 359 is ordinary is a reasonable approximation and even if it later proves to be incorrect, it will not be a source of gross error in the interpretations.

Table 10. Values of the parameters t , V_0 and W_0
for some ordinary leads.

Location	$t(\text{in } 10^9 \text{ yrs.})$	V_0	W_0
Broken Hill*	1.620	0.0652	37.3
Captains Flat**	.335	0.0652	37.2
Cobar**	.321	0.0653	37.1
South-West Finland***	1.801	0.0652	36.9
Sudbury	1.920	0.0654	39.0

* Analyzed by Kollar, Russell and Ulrych (1960)

** Analyzed by R. G. Ostic

*** Analyzed by A. B. Whittles and E. R. Kanasewich

The time t_1 calculated from equations (4) for No. 359 is 1920 million years. This value when substituted in equation (3) gives a time t_2 of 420 million years. The limits of uncertainty of t_1 are not known. Although the values of the lead isotope abundances of No. 359 are precise it is difficult to give an exact age on the basis of one analysis of one sample. A limit of ± 50 million years for t_1 imposes a limit of ± 80 million years on t_2 .

A possible interpretation on the basis of this two-stage model which the writer would like to propose is as follows. Lead mineralization inside the Sudbury Basin occurred approximately 1950 million years ago. A second period of mineralization, in which anomalous lead was emplaced in the Sudbury district occurred during the Appalachian orogeny 350 million years ago.

The time of 1950 million years for the first period of lead mineralization imposes limits on events in the district. If the mineralization was controlled by sedimentary processes, then the lower limit to the Onwatin-Chelmsford sediments inside the Basin is 1950 ± 50 million years. If, on the other hand, the mineralization was contemporaneous with the intrusion of the nickel irruptive, as suggested by Stanton (Stanton and Russell, 1959) the irruptive was intruded approximately 1950 million years ago.

Calculated values for the $\text{Th}^{232}/\text{U}^{238}$ ratio in the second stage, assuming a decay interval from 1950 million years to 350 million years are given in Table 8.

The second interpretation of the history of the Sudbury leads is based on a modified three-stage model. In this case, equations (2) are evaluated for $m = 3$. The condition is imposed, however, that $V_2 = 0$. In other words, from time t_1 , the time of ordinary lead mineralization, to time t_2 of uranium and thorium mineralization, the lead isotope abundances of the ordinary lead were not altered.

Equations (2) become

$$\begin{aligned}x &= a_0 + \alpha V_1 (e^{\lambda t_0} - e^{\lambda t_1}) + \alpha V_3 (e^{\lambda t_2} - e^{\lambda t_3}) \\y &= b_0 + V_1 (e^{\lambda' t_0} - e^{\lambda' t_1}) + V_3 (e^{\lambda' t_2} - e^{\lambda' t_3}) \quad (5) \\z &= c_0 + W_1 (e^{\lambda'' t_0} - e^{\lambda'' t_1}) + W_3 (e^{\lambda'' t_2} - e^{\lambda'' t_3})\end{aligned}$$

The slope R of the straight line in Fig. 19 is given from equations (5) by assuming that V_1 is the same for all samples, but V_3 different for the various samples. Thus

$$R = \frac{e^{\lambda' t_2} - e^{\lambda' t_3}}{\alpha (e^{\lambda t_2} - e^{\lambda t_3})} \quad (6)$$

Equation (6) cannot be solved explicitly for both unknowns. If one chooses a value of either t_2 or t_3 then a value for the other time can be determined. In this case t_3 is the end of the interval during which the radiogenic lead component was generated. In all probability, it can be taken as the time of final mixing and emplacement of the anomalous leads.

For the present interpretation, the writer has chosen a value for t_3 to represent the Grenville orogeny which has affected a large area, including Sudbury, and has been well dated. The value chosen for t_3 , 950 million years, is based on K - Ar and Rb - Sr ages for four gneisses from the Grenville locality (Fairbairn, Hurley and Pinson, 1960). This value is in agreement with many older measurements.

Equation (6) can now be solved and t_2 is calculated to be 1580 ± 50 million years.

The second interpretation which the writer would like to propose is as follows. Lead mineralization inside the Sudbury Basin occurred approximately 1950 million years ago. Uranium and thorium mineralization took place 1580 ± 50 million years ago. A second period of lead mineralization occurred during the formation of the Grenville, 950 million years ago.

There is evidence in Sudbury for an orogeny 1600 million years ago. This evidence is based both on K - Ar and Rb - Sr ages (Faribairn, Hurley and Pinson, 1960). A possible source of uranium and thorium, in the form of radioactive quartz-pebble conglomerates, has been recently described by Thomson (1960). The conglomerates are similar lithologically and lie on the same stratigraphic horizon as uraniferous ores of the Blind River district, dated by Mair et al. (1960) at 1700 ± 100 million years. The distribution of the pebble beds is shown in Fig. 17.

CONCLUSIONS

Although the initial objective of this thesis research was the development of a new technique, the most interesting result has been obtained by applying it to the Sudbury sulphides. The Sudbury area has for a long time been economically one of the most important mining areas of the world, and very few regions have been studied with comparable detail. Despite this, geologists are not in agreement concerning the correct geological interpretation of the observed surface features. The classic interpretation considers the nickel irruptive to be the result of gravity differentiation of a magmatic intrusion into a heavier norite layer at the bottom and a less dense micropegmatite at the top. The resulting intrusive is presumed to have been folded to form the present basin-shaped structure. Thomson (1956), on the other hand, considers the irruptive to have been a two-stage intrusion. Another suggestion has been that the micropegmatite is the granitization product of the overlying sediments. The existence of these widely differing hypotheses is an indication of the geological complexity of the region.

The reason for the complexity seems almost certainly related to the fact that Sudbury lies close to the boundary of two geological provinces of vastly different age.

Kanasewich (1962) has suggested that near Sudbury, there occurs the junction of four younger geological provinces with the older Superior province. This suggestion is certainly in accord with the observation that conventional age determination methods give a more confused pattern here than for any other areas yet studied. Analyses reported in the literature include age determinations based on many of the common dating methods. These include potassium-argon and rubidium-strontium ages for biotites and potassium feldspars, whole rock rubidium-strontium ages, as well as the earlier common lead isotope determinations. The results have been mostly confused and difficult to interpret. Typical of these are the analyses of Fairbairn, Hurley and Pinson (1960) who have plotted their values as shown in Fig. 21. This figure shows clearly the difficulty in picking significant events. The problem does not become easier if only analyses of a single formation are considered. The solid bars in Fig. 21 show measurements for samples of the Copper Cliff rhyolite obtained at two localities. The above authors have suggested a chronological history for the area based in part on these data, but this has involved the selection of critical results on the basis of prior experience. Hurley has coined the term "orogenic noise" to describe this type of age assemblages.

A closer inspection of the available data does suggest that at least one event is significant. This occurred at

Fig. 21. Histogram of K - Ar and Rb - Sr ages from Sudbury (Fairbairn, Hurley and Pinson, 1960)

about 2050 ± 100 million years, and is indicated by whole rock rubidium-strontium ages on the Murray and Creighton granites. The rubidium-strontium data on associated minerals suggest that major metamorphic events may have occurred at about 1600 million years and about 1200 million years ago, but these are less certain. These conclusions are the result of more than 54 separate age determinations.

Now that the quantitative interpretation of the isotope ratios of multi-stage leads has been reasonably well worked out (Kanasewich, 1962), it is appropriate to try to apply it to this area for which the history has been so complex. The analyses and interpretations were discussed fully in Chapter IV. The significant fact is that the analyses made follow the very simple linear relationship that is characteristic of anomalous leads of a two-stage history. That is, even in this complex situation, the lead isotope ratios exhibit a simple pattern.

The closeness of fit of the points to their best straight line shows that the slope of the line must be determined by only two events. There are only two likely periods to which the younger of these events can be assigned. These are the Appalachian and Grenville orogenies. This determines the older event as either 1950 million years or 1600 million years, respectively. The latter interpretation is favoured because there is no evidence that the Appalachian orogeny

influenced this region, and because of the independent evidence for the 1600 million year event.

In many respects these measurements are the most interesting result of the research. However they could not have been obtained without the development of the free radical preparation of tetramethyllead. Conventional techniques would have restricted the samples studied to galenas. The University of Toronto analyses indicate that the isotope ratios for galenas are clustered about two points. The better sampling possible by using different sulphides has resulted in points which lie evenly distributed along the anomalous lead line. This distribution helps to establish the validity of the interpretations.

The same analyses could have been made, of course, using solid source mass spectrometry. Published analyses suggest that this technique would have yielded less precise values. Data from a recent study on a suite of galenas from the Dominion Reef, Witwatersrand (Burger, Nicolaysen and De Villiers, 1962) is plotted in Fig. 22 where it can be seen that the scatter of points is much greater than for the analyses carried out here. Expressed as a standard deviation in the Pb^{207}/Pb^{204} ratio the scatter for the Dominion Reef analyses is 1.75% compared with 0.37% for the Sudbury sulphides. Presumably the scatter would not be smaller for

Fig. 22. Pb^{207}/Pb^{204} plotted against Pb^{206}/Pb^{204} for Dominion Reef galenas and for Sudbury sulphides (Burger, Nicolaysen and De Villiers, 1962)

samples containing much less lead. For the present study, had the scatter been as large as 1.75%, it would have been impossible to exclude multi-stage growth processes.

Finally, the principle contributions of this thesis are considered to be two in number. The first is the development of a new technique for the synthesis of tetramethyllead which has substantially reduced the required sample size and has considerably extended the range of minerals which may be studied with a gas source mass spectrometer. The second is the presentation of new data which has significant bearing on the sequence of geological events in the Sudbury district.

APPENDIX

The Plate theory in gas chromatography (Keulemans, 1957, Martin and Synge, 1941)

X_{Lp} = concentration of solute in liquid in vessel p

X_{Gp} = concentration of solute in gas in vessel p

V_G = volume of inert gas phase per vessel

V_L = volume of non-volatile liquid per vessel

k = partition coefficient

V = volume of gas flow

Fig. A1. Three successive adsorption vessels.

The following assumptions are involved:

(i) The volumes of gas G and liquid L are equal in each vessel and remain constant throughout.

(ii) The distribution isotherm is linear.

The processes of distribution of the solute through the column which is considered to be made up of n ($n=0,1,2,\dots$) adsorption vessels is as follows:

The solute is introduced into vessel number 0 where it dissolves in the non-volatile liquid L and exerts a vapour pressure above it. The carrier gas then carries the vapours into the next vessel. This process, illustrated in Fig. A1, is then repeated.

If volume dV of gas passes from vessel $p-1$ to p , the amount of solute transferred is $X_G(p-1)dV$. Similarly, the amount of solute transferred from vessel p to $p+1$ is $X_G(p)dV$.

A change of solute concentration occurs, dX_L in the liquid phase and dX_G in the gas phase.

Therefore, change of amount of solute in gas phase at vessel $p = dX_{Gp}V_G$ and in the liquid phase $= dX_{Lp}V_L$.

A material balance requires that

$$(X_G(p-1) - X_G(p))dV = V_G dX_{Gp} + V_L dX_{Lp} .$$

The equilibrium condition is $X_{Lp} = kX_{Gp}$.

Eliminating X_{Lp}

$$\frac{dX_{Gp}}{dV} = \frac{X_{G(p-1)} - X_{Gp}}{V_G + kV_L} \quad \text{..... A}$$

Initial conditions are that the solute is introduced into the first vessel only, where the respective concentrations are X_{L0} and X_{G0} .

Let

$$v = \frac{V}{V_G + kV_L} = \frac{V}{\text{effective plate volume}}$$

Then, solution of equation A is

$$X_{Gp} = \frac{X_{G0} e^{-v} \cdot v^p}{p!}$$

If

$$x_p = \frac{X_{Gp}}{X_{G0}}$$

the equation of the elution curve is

$$x_p = \frac{e^{-v} \cdot v^p}{p!}$$

The elution curve is shown in Fig. A2.

At this point the writer has extended the mathematical treatment of Keulemans (1957), by developing the subsequent expressions.

Fig. A2. Elution curve.

Maximum of peak occurs at

$$\frac{dx_p}{dv} = \frac{-e^{-v}v^p}{p!} + \frac{e^{-v}pv^{p-1}}{p!} = 0$$

Therefore the maximum occurs at $v = p$

Inflection points of the peak occur at $\frac{d^2x_p}{dv^2} = 0$

or

$$\frac{e^{-v}v^p}{p!} - \frac{e^{-v}pv^{p-1}}{p!} - \frac{e^{-v}pv^{p-1}}{p!} + \frac{e^{-v}p(p-1)v^{p-2}}{p!} = 0$$

Hence

$$v^2 - 2pv + p(p-1) = 0$$

and therefore inflection points occur at

$$v = p \pm \sqrt{p}$$

The tangents through the inflection points E_1 and E_2 cut the base line at B and D.

Let $AB = c$

Equation of BE_1 is

$$v = mx_p + c$$

At point E_1

$$p - \sqrt{p} = \frac{p! e^{p-\sqrt{p}}}{(p-\sqrt{p})^p \left(\frac{p}{p-\sqrt{p}} - 1 \right)} \cdot e^{-(p+\sqrt{p})} \cdot \frac{(p-\sqrt{p})^p}{p!} + c$$

Therefore

$$p - \sqrt{p} = \frac{p - \sqrt{p}}{\sqrt{p}} + c$$

Consequently

$$c = AB = 1 + p - 2\sqrt{p}$$

Similarly

$$AD = 1 + p + 2\sqrt{p}$$

Therefore, peakwidth

$$BD = \omega = 4\sqrt{p}$$

For large p , distribution becomes Gaussian and in

chromatographic processes, where the column has n plates, the equation of the elution curve becomes

$$x_n = \frac{e^{-v} v^n}{n!}$$

The peak maximum occurs at $v = n$ and breaks through after a gas volume equal to $V_R = n(V_G + kV_L)$.

V_R is called the retention volume of the particular component.

For large n , nV_G is the gas hold up of the column
 nV_L is the liquid hold up of the column

Number of theoretical plates

Let d be the distance from the injection point to the projection of the peak maximum onto the base line.

Let ρ be a proportionality factor

then $d = \rho n$ and $\omega = \rho 4 \sqrt{n}$

The number of theoretical plates is therefore given by

$$n = \left(\frac{4d}{\omega} \right)^2$$

The Rate theory in gas chromatography
(Van Deemter, Zuiderweg and Klinkenberg, 1956; Keulemans, 1957)

The mathematical development is involved and only a very brief treatment is presented.

Considering the material balance per unit cross sectional area shown diagrammatically in Fig. A3:

$$F_{\text{gas}} \frac{\partial C_{\text{gas}}}{\partial t} = D_{\text{eff}} F_{\text{gas}} \frac{\partial^2 C_{\text{gas}}}{\partial x^2} - u F_{\text{gas}} \frac{\partial C_{\text{gas}}}{\partial x} + \alpha \left(C_{\text{liq}} - \frac{C_{\text{gas}}}{k} \right)$$

This equation states that

Change of amount of component in length Δx = Amount of component transported by (longitudinal diffusion + convection + mass transfer)

Similarly for the liquid phase

$$F_{\text{liq}} \frac{\partial C_{\text{liq}}}{\partial t} = \alpha \left(\frac{C_{\text{gas}}}{k} - C_{\text{liq}} \right)$$

The solution of these equations is performed with the aid of the general solution of Lapidus and Amundson (1952). The solution is long and tedious and no purpose would be served by repeating it here.

A simplification is introduced by reducing the solution

where F_{gas} = volume fraction of gas in the column
 F_{liq} = volume fraction of liquid in the column
 C_{gas} = solute concentration in the gas phase
 C_{liq} = solute concentration in the liquid phase
 D_{eff} = effective longitudinal diffusivity
 u = linear gas velocity
 k = partition coefficient
 α = mass transfer coefficient
 x = distance along the column

Fig. A3. Material balance in a continuous column.
 (after Keulemans, 1957)

to a Gaussian function. This is in order if the column contains a large number of plates. The Gaussian solution is combined with the Gaussian distribution for the plate theory to give the Van Deemter rate equation

$$\text{H.E.T.P.} = 2\lambda d_p + \frac{2\gamma D_{\text{gas}}}{u} + \frac{8}{\pi^2} \frac{k'}{(1+k')^2} \frac{d_f^2}{D_{\text{liq}}} \cdot u$$

The symbols used in this equation are defined as follows:

H.E.T.P. = Height equivalent to a theoretical plate

λ = measure of packing irregularities

d_p = particle diameter

γ = tortuosity factor

u = gas velocity

k' = extraction coefficient

d_f = statistical average of liquid film thickness

D_{gas} = molecular diffusivity in gas

D_{liq} = molecular diffusivity in liquid.

BIBLIOGRAPHY

- Ahrens, L.H. The use of ionization potentials. Part 2.
Anion affinity and geochemistry. *Geochim. et Cosmochim. Acta.* 3, 1, 1953.
- Aston, F.W. The isotopic constitution and atomic weight of lead. *Proc. Roy. Soc. Lond.* 140A, 535, 1933.
- Auger, P.E. Zoning and district variations of the minor elements in pyrite of Canadian gold deposits.
Econ. Geol. 56, 401, 1941.
- Barnard, G.P. Modern mass spectrometry. London: The Institute of Physics. 1953.
- Bazinet, M.L. and Walsh, J.T. Combination gas sampler and fraction collector for gas chromatography and mass spectrometer application. *Rev. Sci. Inst.* 32, 346, 1960.
- Bell, E.R., Raley, J.H., Rust, F.F., Senbold, F.H., and Vaughan, W.E. Reactions of free radicals associated with low temperature oxidation of paraffins.
Faraday Soc. Discussions 10, 242, 1951.
- Benson, S.W. The foundations of chemical kinetics.
McGraw-Hill. New York. 1960.
- Beynon, J.H. Mass spectrometry and its applications to organic chemistry. Elsevier Publishing Co. New York. 1960.

- Burger, A.J., Nicolaysen, L.O. and De Villiers, J.W. Lead isotopic compositions of galenas from the Witwatersrand and Orange Free State, and their relation to the Witwatersrand and Dominion Reef uraninites. *Geochim. et Cosmochim. Acta.* 26, 25, 1962.
- Coates, G.E. *Organo metallic compounds.* John Wiley and Sons Inc. New York, 1960.
- Collins, C.B., Freeman, J.R., and Wilson, J.T. A modification of the isotopic lead method for the determination of geologic ages. *Phys. Rev.* 82, 966, 1951.
- Collins, C.B., Farquhar, R.M. and Russell, R.D. Isotopic constitution of radiogenic leads and the measurement of geological time. *Bull. Geol. Soc. Amer.* 65, 1, 1954.
- Davis, G.L., Tilton, G.R., Aldrich, L.T., Wetherill, G.M., and Faul, H. The age of rocks and minerals. *Carn. Inst. Washington Year Book.* 56, 164, 1957.
- Deemter, J.J. van, Zuiderweg, F.J. and Klinkenberg, A. Longitudinal diffusion and resistance to mass transfer as causes of non ideality in chromatography. *Chem. Eng. Sci.* 5, 271, 1956.
- Dempster, A.J. A new method of positive ray analysis. *Phys. Rev.* 11, 316, 1918.

- De Wet, W.J. and Pretorius, V. Factors influencing the efficiency of gas-liquid partition chromatography. Anal. Chem. 30, 325, 1958.
- Diebler, V.H. and Mohler, F.L. Mass spectra of some organo-lead and organo-mercury compounds. Jour. Res. Natl. Bur. Standards, Washington. 47, No. 5, 337, 1951.
- Doty, W.R. and Ryason, P.R. Greaseless vacuum valve useful in kinetic studies. Rev. Sci. Inst. 32, 89, 1961.
- Duckworth, H.E. Mass Spectroscopy. Cambridge University Press. 1958.
- Ehrenberg, H.F., Geiss, I. and Taubert, R. A high precision mass spectrometer for lead isotopes. Z. angew. Phys. 7, 416, 1955.
- Fairbairn, H.W., Hurley, P.M. and Pinson, W.H. Mineral and rock ages at Sudbury-Blind River, Ontario. Proc. Geol. Assoc. Can. 12, 41, 1960.
- Farquhar, R.M. and Russell, R.D. Anomalous leads from the upper Great Lakes region of Ontario. Trans. Amer. Geophys. Un. 38, 552, 1957.
- Fleischer, M. Minor elements in some sulphide minerals. Econ. Geol. 50th Anniv. Vol. 970, 1955.
- Gallo, G. and Del Guerra, M. The reaction of hydrogen with metallic oxides and sulphides. VI. Ann. Chim. (Rome) 41, 51, 1951.

- Gilman, H. and Jones, R.G. Reactions of metallic thallium and metallic lead with organic halides. J. Amer. Chem. Soc. 72, 1760, 1950.
- Glueckauf, E. Theory of chromatography Part 9. The "theoretical plate" concept in column separations. Trans. Faraday Soc. 51, 34, 1955.
- Hausdorff, H.H. and Brenner, N. Gas Chromatography. Part 3. The Oil and Gas Jour. 56, 86, 1958.
- Hawley, J.E. and Nichol, I. Trace elements in pyrite, pyrrhotite and chalcopyrite of different ores. Econ. Geol. 56, 467, 1961.
- Jones, L.W. and Werner, L. Hydrocarbon bases and a study of organic derivatives of mercury and of lead. Journ. Am. Chem. Soc. 40, 1257, 1948.
- Kanasweich, E.R. Approximate age of tectonic activity using anomalous lead isotopes. Geophysical Journal (in press) 1962.
- Kanasewich, E.R. Quantitative interpretations of anomalous lead isotope abundances. Ph.D. Thesis, Department of Physics, University of British Columbia, 1962.
- Kaufman, H.C. Handbook of organo metallic compounds. D. Van Nostrand Co., New Jersey. 1961.

Keulemans, A.I. Gas Chromatography. Reinhold, New York 1957.

Kollar, F. The precise intercomparison of lead isotope ratios. Ph.D. Thesis, Department of Physics, University of British Columbia, 1960.

Kollar, F., Russell, R.D., and Ulrych, T.J. Precise inter-comparison of lead isotope ratios: Broken Hill and Mount Isa. Nature. 187, 754, 1960.

Lapidus, L. and Amundson, N.R. The rate determining steps in radical adsorption analysis. J. Phys. Chem. 56, 373, 1952.

Leermakers, J.A. Formation of methyl radicals in the decomposition of azomethane. Jour. Am. Chem. Soc. 55, 3499, 1933.

Mair, J.A. Solid source mass spectrometry: applications to geochronology. Ph.D. Thesis, Department of Physics, University of Toronto, 1958.

Mair, J.A., Maynes, A.D., Patchett, J.E. and Russell, R.D. Isotopic evidence on the origin and age of the Blind River uranium deposits. J. Geophys. Research 65, 341, 1960.

Marshall, R.R. and Hess, D.C. Determination of very small quantities of lead. Anal. Chem. 32, 960, 1960.

- Martin, A.J. and Synge, R.L. A new form of chromatogram employing two liquid phases. I. A theory of Chromatography. Biochem. J. 35, 1358, 1941.
- Murthy, R.V. and Patterson, C.C. Lead isotopes in ores and rocks of Butte, Montana. Econ. Geol. 56, 59, 1961.
- Murthy, R.V. and Patterson, C.C. Primary isochron of zero age for meteorites and the earth. J. Geophys. Research 67, 1161, 1962.
- Nier, A.O. Variation in the relative abundances of the isotopes of common lead from various sources. Jour. Am. Chem. Soc. 60, 1571, 1938.
- Nier, A.O. The isotopic constitution of radiogenic leads and the measurement of geologic time. II. Phys. Rev. 55, 153, 1939.
- Norrish, R.G., Crone, G.H. and Saltmarsh, O.D. Primary photochemical reactions. Part V. The spectroscopy and photochemical decomposition of acetone. J. Chem. Soc. Part 2. 1456, 1934.
- Paneth, F. and Hofeditz, W. Preparation of free methyl. Ber. 62B, 1335, 1929.
- Paneth, F. and Lautsch, W. Free organic residues in the gaseous state. III. The mechanism of the reaction of the free radicals. Ber. 64B, 2708, 1931.

- Patterson, C.C. The isotopic composition of meteoric, basaltic and oceanic leads and the age of the earth. Proc. First Conf. on Nuclear Processes in Geological Settings. 36, 1953.
- Rice, F.O. Decomposition of organic compounds into free radicals. Trans. Faraday Soc. 30, 152, 1934.
- Rice, F.O. and Rice, K.K. The aliphatic free radical. Baltimore. 1935.
- Richards, J.R. Isotopic composition of Australian leads. 2. Experimental procedures and interlaboratory comparisons. J. Geophys. Research 67, 869, 1962a.
- Richards, J.R. Isotopic composition of Australian leads. 1. Preparation of tetramethyllead samples. Microchimica Acta (In press). 1962b.
- Russell, R.D., Farquhar, R.M., Cumming, G.L. and Wilson, J.T. Dating galenas by means of their isotopic constitutions. Trans. Amer. Geophys. Un. 35, 301, 1954.
- Russell, R.D., Kanasewich, E.R. and Ozard, J.M. Isotopic abundances of lead from a frequently mixed source. Geochim. et Cosmochim. Acta (In press). 1962.
- Russell, R.D. and Farquhar, R.M. Lead Isotopes in Geology. Interscience Publishers. New York. 1960.

Russell, R.D., Ulrych, T.J. and Kollar, F. Anomalous leads from Broken Hill, Australia. J. Geophys. Research. 66, 1495, 1961.

Russell, R.D. and Slawson, W.F. Age of the Cuddaphas, India. Nature. 194, 565, 1962.

Stanton, R.L. and Russell, R.D. Anomalous leads and the emplacement of lead sulphide ores. Econ. Geol. 54, 588, 1959.

Steacie, E.W. Atomic and free radical reactions. Vol. I. Reinhold, New York 2nd ed. 1954.

Surkan, A.J. Sources of lead ions for mass spectrometry. M.A. Thesis, Department of Physics, University of Toronto. 1956.

Thomson, J.E. Geology of the Sudbury Basin. Ont. Dept. Mines. LXV Part 3. 1956.

Thomson, J.E. Uranium and thorium deposits at the base of the Huronian system in the district of Sudbury. Ont. Dept. Mines. Geol. Report 1. 1960.

Tilton, G.R., Patterson, C.C., Brown, H., Inghram, M.C., Hayden, R.J., Hess, D.C. and Larsen, E.S. Jr. Isotopic composition and distribution of lead, uranium and thorium in a precambrian granite. Bull. Geol. Soc. Amer. 66, 1131, 1955.

Trotman-Dickenson, A.F. Free Radicals: An Introduction.

John Wiley and Sons Inc. New York. 1959.

Ulrych, T.J. The preparation of lead tetramethyl for mass spectrometer analysis. M.Sc. Thesis, Department of Physics, University of British Columbia. 1960.

Waters, W.A. The chemistry of free radical reactions. Oxford, London 2nd ed. 1935.

Wetherill, G.W., Davis, G.L. and Tilton, G.R. Age measurements on minerals from the Cutler Batholith, Cutler, Ontario. J. Geophys. Research. 65, 2461, 1960.