THE PREPARATION OF LEAD TETRAMETHYL

for

MASS SPECTROMETER ANALYSIS

by

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ABSTRACT

This thesis is concerned with the problems of sample preparation arising in the study of lead isotope abundances. The importance of this study to geophysics has been amply shown by R.D. Russell, R.M. Farquhar, F.G. Houtermans, J.T. Wilson, H.F. Ehrenberg and many others.

Chapter 1 gives an outline of lead isotope measurement techniques, including types of mass spectrometers generally used and some of the problems encountered. The mass spectrometer used in the present research was designed and constructed by R.D. Russell and F. Kollar and descriptions of it will be found in their publications and in F. Kollar's Ph.D. thesis. The present techniques of producing lead tetramethyl for isotopic analysis from ore samples are discussed in Chapter 2.

The remaining chapters deal with the purification of lead tetramethyl for mass spectrometer analysis, using vapour phase chromatography. This technique has found immediate application in the precise intercomparison of lead samples recently carried out in the Geophysics Laboratory at the University of British Columbia by F. Kollar and others (F. Kollar, R.D. Russell and T.J. Ulrych, in press). The long range object for developing this technique is to purify lead tetramethyl prepared by free methyl radicals reacting with metallic lead (cf. A.J. Surkan 1956) prior to isotopic analysis. The presence of impurities in samples prepared this way has

discouraged the development of this method in the past. The final chapter deals with this aspect of the proposed problem.

This thesis is intended as a preliminary to the writer's Ph.D. research which will also deal with isotopic lead analysis.

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CHAPTER 1

Lead Isotope Abundances.

The isotopic composition of lead in lead ores is extremely variable. During the past six or seven years, the nature of this variation has been the subject of extensive investigation. Broadly speaking, there are two objectives of such a study.

Firstly, a properly formulated model to explain these variations will aid in understanding the geochemical processes involving lead, uranium and thorium in the evolution of the outer parts of the earth. Secondly, it is desirable to determine some of the geological aspects of lead ore formation.

It is not the aim of the writer to give an exhaustive treatment of the subject. Therefore the following summary is greatly condensed.

Most elements found in nature consist of varying mixtures of different isotopes. The variations in the isotope proportions are due mainly to two processes. The first is due to fractionation, accompanying natural chemical and physical processes, and the second is the addition of daughter elements from radioactive decay.

The element lead has four stable isotopes of atomic mass 204, 206, 207 and 208. All four of these isotopes are found in lead minerals in greatly varying proportions. Because of the relatively high atomic weight of lead, the

FIG I.I.

FIG I.I (a) COMMON AND RADIOGENIC
LEAD
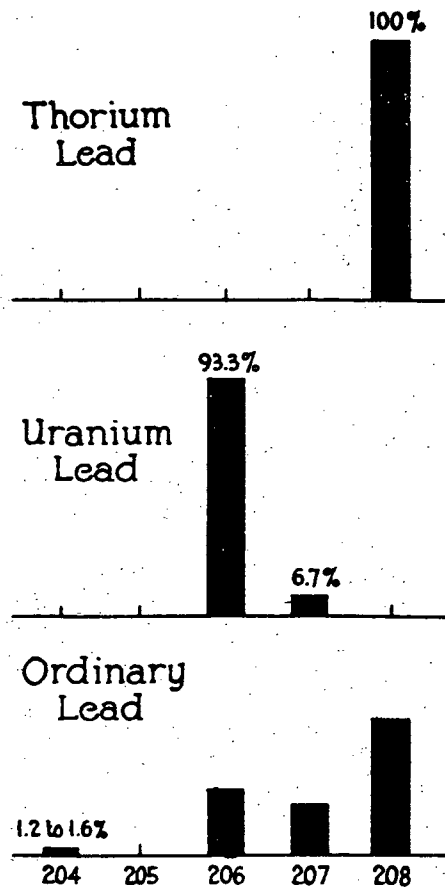
FIG I.I (b) URANIUM AND THORIUM DECAY
SCHEMES

TO FOLLOW P. I
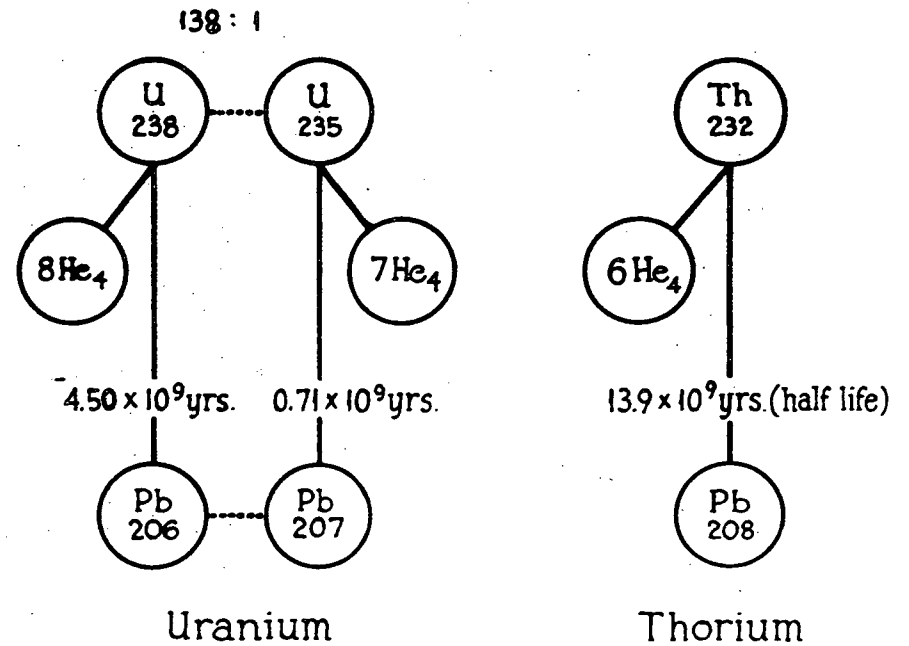
first process mentioned above has never been observed in nature and is quite difficult to achieve in the laboratory (Russell 1959). The variations in the lead isotope ratios are, therefore, explained by the second process. It is known that lead-206, lead-207 and lead-208 are identical with the lead produced in the radioactive decay of uranium-238, uranium-235 and thorium-232 respectively and therefore the addition of radiogenic lead to the mineral lead will increase the amount of lead-206, lead-207 and lead-208 relative to lead-204 (Fig. 1.1 (a) and (b)).

An excellent example of the application of lead isotope ratios has been given recently by Stanton and Russell (Stanton and Russell 1959) with regard to lead sulphide ores.

They studied a certain class of conformable lead sulphide ore and found that the isotope ratios of such deposits are very uniform and simply related, while the isotope ratios of certain vein deposits contain anomalous additions of radiogenic leads. These results support the hypothesis that these conformable deposits are the product of a subcrustal source and have been in contact with crustal rocks for only a short time before deposition. The vein deposits, on the other hand, seem to have migrated through significant thicknesses of older crustal rocks.

The beginning of absolute geological age determinations based on radioactive decay can be traced to Rutherford and Soddy (Wilson, Russell and Farquhar 1956, p. 295),

who put forward the hypothesis that lead isotopes are formed by means of uranium and thorium decay. The standard methods used for this work are those based on the decay of the two isotopes of uranium and the one isotope of thorium. The reasons for this choice are clear.

1). All three isotopes are radioactive and therefore three ages can be obtained as a check for consistency.

2). The decay schemes are well known.

3). The parents are highly concentrated in minerals like uraninite, which are formed with negligible amounts of lead.

The early work in age determination was done through chemical analyses (Ellsworth 1932, Holmes 1937). It was found however that there was an uncertainty due to common lead contamination, and an isotopic analysis, as well as a chemical analysis is now made. The proportion of common lead contamination is inferred from the abundance of lead-204.

One age value can be obtained from the isotopic analysis alone using the equation (Nier 1939)

$$\frac{Pb^{207}}{Pb^{206}} = \frac{U^{235}}{U^{238}} \frac{(e^{\lambda^1 t} - 1)}{(e^{\lambda t} - 1)}$$

where λ and λ^1 are the decay constants of uranium-238 and uranium-235, $\lambda = 0.153_7 \times 10^{-9}$ yrs.$^{-1}$, $\lambda^1 = 0.972_2 \times 10^{-9}$ yrs.$^{-1}$ (Fleming, Ghiorso and Cunningham 1951 and 1952), t is the age. $U^{235} : U^{238} = 1 : 137.8$ (Inghram 1947).

The analysis of lead isotopes is performed with the

aid of a mass spectrometer, whose basic operation is as
follows.

Ions are formed from the sample to be analysed either
by electron bombardment or by evaporation from a hot fila-
ment. The ions leave the ionisation chamber through a
narrow slit, are accelerated to a fixed energy by a strong
electrostatic field and pass through collimating slits. A
magnetic field parallel to the slits diverts the ions into
circular paths, the radii of which depend on the momentum
of the ions. Thus sorted, the ions of a certain mass pass
through resolving slits and strike a collector. The charge
given up by the ions at the collector produces an electric
current which is amplified and recorded. By varying the
magnetic field, the complete mass spectrum of the sample
is obtained.

In the solid source mass spectrometer, the sample is
introduced into the ionisation chamber in the form of a
solid, usually by being painted on a tungsten filament
from which it is evaporated. In the gas source instrument,
the sample is introduced in a gaseous form and is bombarded
with electrons.

For routine analysis, the gas source mass spectrometer
has several advantages over the solid source instrument,
the main one being the ease of operation. In the solid
source mass spectrometer the introduction or removal of a
sample usually necessitates breaking the vacuum, whereas
this is not necessary in the former type. Another im-
portant factor is the reproducibility of results; the

solid ion source gives widely varying ion efficiencies in some cases (Mair 1958).

In analysis of lead isotopes the solid source mass spectrometer offers one important advantage. In some lead-bearing minerals, e.g. zircons, apatites, feldspars, the lead is present in very small amounts, ranging upward from one part per million. Because the minimum sample size which can be readily handled using the classical gaseous techniques is of the order of 10 mg. (Collins, Freeman and Wilson 1951, and Collins, Russell and Farquhar 1953) (see Chapter 2) it would be necessary to process several kilograms of the sample in order to obtain sufficient lead from the mineral. By using a surface ionisation source, however, good results have been obtained for mineral separates from granites (Tilton et al. 1955) and a sample containing as little as 2μg. of lead has been reasonably well analysed (Mair 1958).

The problem which the writer has undertaken is the extension of the range of application of the gas source mass spectrometer to studies of lead isotopes in minerals in which the lead is contained as a minor constituent. The first stages of this problem formed a basis of the writer's M.Sc. research.

CHAPTER 2

The Lead Tetramethyl Technique.

The first mass spectrographic studies of lead were made
by F.W. Aston (1933) who utilized a discharge through lead
tetramethyl vapours in a discharge tube. In his extensive
studies of the isotopic composition of lead, Nier (1938,
1939, Nier, Thompson and Murphey 1941) used a method in which
lead iodide was evaporated in the vacuum system of a gas
source mass spectrometer. This method, however, suffers
from several disadvantages. Since lead iodide is a solid,
both source and tube must be heated to 350°C to give suf-
ficient vapour pressure. Free lead is deposited on the in-
side of the mass spectrometer tube giving rise to electrical
leakage and there may also be a memory effect. Thus fre-
quent and troublesome cleaning is necessary making the rate
at which samples can be analysed rather slow. Another dis-
advantage is that if mercury diffusion pumps are used, the
Pb^+ spectrum is complicated by the mercury isotope of mass
204. The PbI^+ ions can be used for analysis but the
resolution required is fifty percent higher than in the
previous case. Oil pumps may reduce the first limitation
but the advantage is partially cancelled by the variable
hydrocarbon background.

Because of the above difficulties, C.B. Collins in
1951 turned back to a lead tetramethyl technique.

On bombardment with 50-150 volt electrons, lead

FIG 2.I.

Normal Lead Tetramethyl Spectrogram

Sample source : Ethyl Corporation, Detroit

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FIG 2.2.

Radiogenic Lead Tetramethyl Spectogram
Congo pitchblende

Age: 6.30×10^8 years

$Pb(CH_3)_3^+$

$Pb(CH_3)_1^+$

$Pb(CH_3)_2^+$

Pb^+

252 251

237 236

222 221 220 219

207 206
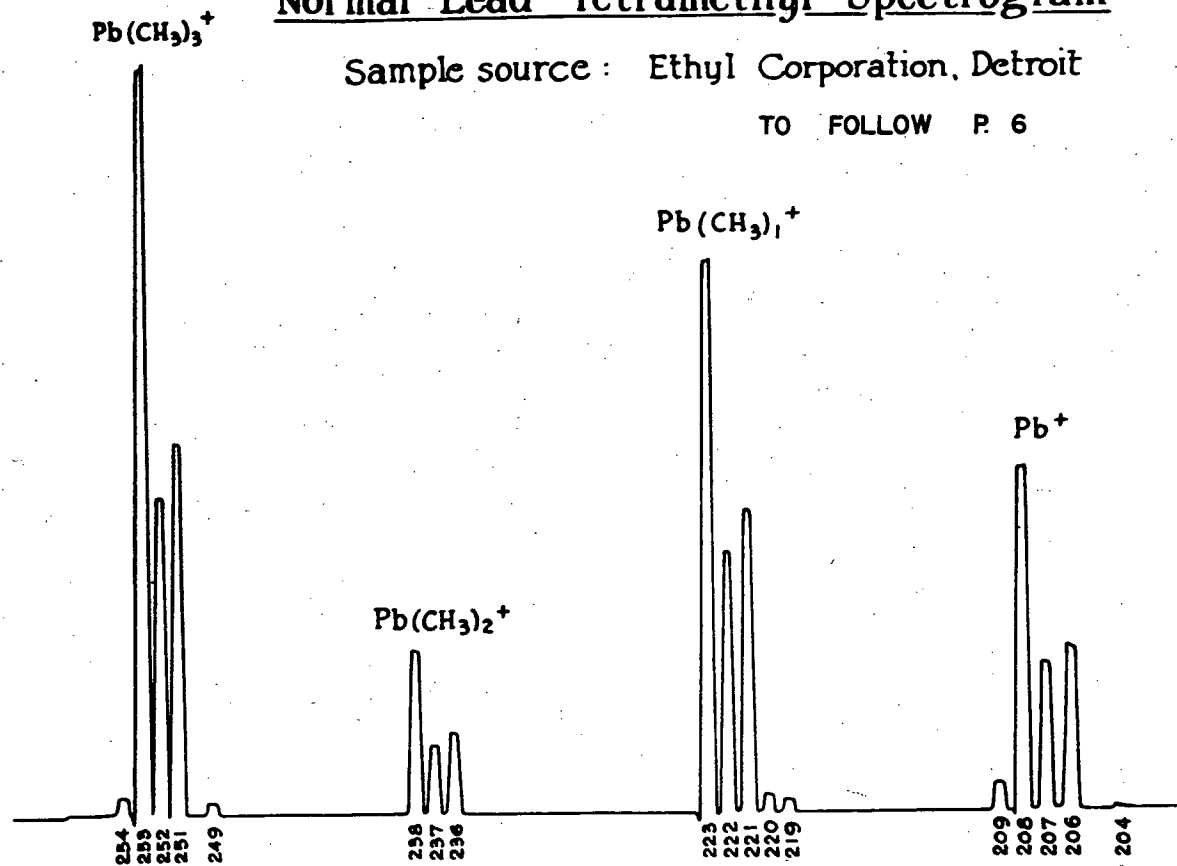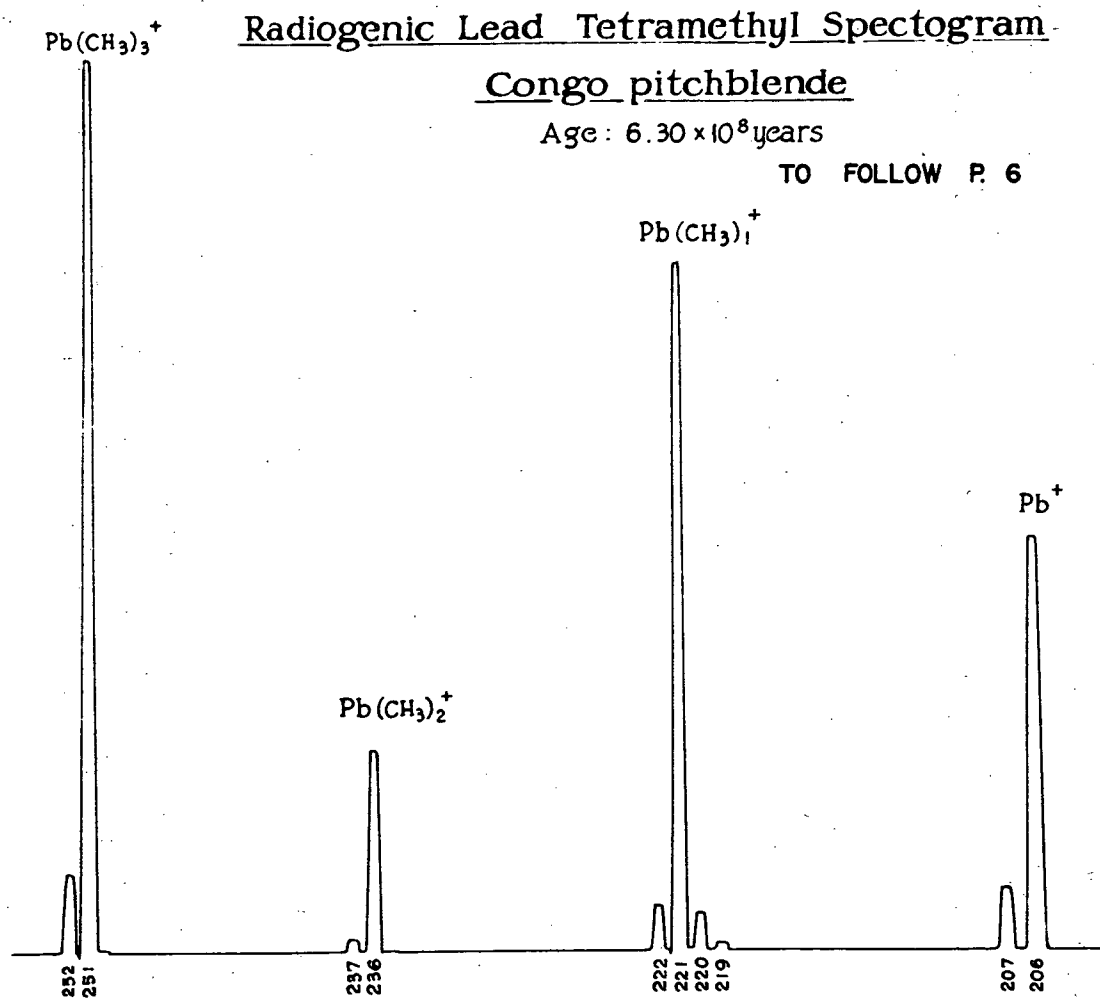
tetramethyl dissociates into the following ion groups. Pb^+, $Pb(CH_3)_2^+$, $Pb(CH_3)_3^+$ and a small proportion of $Pb(CH_3)_4^+$. Collins, Russell and Farquhar (1953) and Diebler and Mohler (1951) have reported the abundances of ions observed from lead tetramethyl. The magnitudes of the abundances of PbH^+ ions and the effect of C^{13} in the $Pb(CH_3)_3^+$ spectrogram obtained in the two laboratories are not in close agreement. The variation in the two determinations is probably due to different ion source conditions.

Fig. 2.1 and Fig. 2.2 show spectrograms for ordinary and radiogenic lead respectively. The most useful spectrograms for calculating the abundances of lead isotopes are those of the Pb^+ and $Pb(CH_3)_3^+$ ion groups. Interpretation of the different ion groups is complicated by the presence of hydrides, the loss of one, two or three hydrogen atoms and by the carbon-13 effect.

The analysis of the Pb^+ spectrogram can best be illustrated by Table 2.1 which shows the contribution of the PbH^+ ions to the interesting mass numbers and Table 2.2 which also shows the calculated relative abundances of the four lead isotopes from the Pb^+ ion spectrogram. From the figures in these tables it is possible to calculate the signal obtained from the PbH^+ ion group. In this case it comes to 8.3 percent of the total ion signal from the Pb^+ ion group.

Several disadvantages present themselves if the Pb^+ ion spectrogram is used for measuring the abundances of

TABLE 2.1

PbH$^+$ EFFECT IN THE Pb$^+$ SPECTROGRAM

Mass number	Ions
204	Pb^{204}
205	Pb^{204}H
206	Pb^{206}
207	Pb^{207} + Pb^{206}H
208	Pb^{208} + Pb^{207}H
209	Pb^{208}H

TABLE 2.2

RELATIVE ISOTOPIC ABUNDANCES FROM THE Pb$^+$ SPECTROGRAM

Mass number	Relative intensity	Lead isotope	Relative abundance, %
204	1.448 $\pm$ 0.003	204	1.574 $\pm$ 0.005
205	0.135 $\pm$ 0.003		
206	20.31 $\pm$ 0.02	206	22.07 $\pm$ 0.03
207	23.23 $\pm$ 0.02	207	23.33 $\pm$ 0.03
208	50.65 $\pm$ 0.03	208	53.02 $\pm$ 0.05
209	4.23 $\pm$ 0.01		

the isotopes of lead. The PbH^+/Pb^+ fraction depends on the energy of the ionising electrons and on the temperature of the ion source, both of which may vary. Secondly, the iso- tope mercury-204 which results from the use of mercury diffusion pumps complicates the quantitative determination of lead-204. In the analysis of radiogenic lead, because of the very small lead-204 and very variable lead-208 contents, no direct measure of the PbH^+ contribution may be possible.

Tables 2.3 and 2.4 illustrate the analysis of a typical $Pb(CH_3)_3^+$ ion spectrogram. Corrections have been made for the carbon-13 effect and the loss of one hydrogen atom. From the numbers in these tables it can be shown that the contribution of the $Pb(C_3H_8)^+$ ions amounts to 0.8% of that from the $Pb(C_3H_9)^+$ ions. The major cor- rection to be applied is that for carbon-13 and is not dependent on the energy of the ionising electrons or the temperature of the ion source.

Because of the above mentioned advantages and be- cause it is the most abundant, the $Pb(CH_3)_3^+$ ion group spectrogram is preferred to the Pb^+ ion group spectrogram, when sufficient resolution of the mass spectrometer is available.

Jones and Werner (1918) have described the synthesis of lead tetramethyl from lead chloride and Grignard re- agent. (The term Grignard reagent refers to any solution

TABLE 2.3

C^{13} AND $Pb(C_3H_8)^+$ EFFECTS IN THE $Pb(CH_3)_3^+$ SPECTROGRAM

Mass number	Ions
248	$Pb^{204}(C^{12}H_3)_2(C^{12}H_2)$
249	$Pb^{204}(C^{12}H_3)_3$
250	$Pb^{204}(C^{12}H_3)_2(C^{13}H_3) + Pb^{206}(C^{12}H_3)_2(C^{12}H_2)$
251	$Pb^{206}(C^{12}H_3)_3 + Pb^{207}(C^{12}H_3)_2(C^{12}H_2)$
252	$Pb^{207}(C^{12}H_3)_3 + Pb^{206}(C^{12}H_3)_2(C^{13}H_3) + Pb^{208}(C^{12}H_3)_2(C^{12}H_2)$
253	$Pb^{208}(C^{12}H_3)_3 + Pb^{207}(C^{12}H_3)_2(C^{13}H_3)$
254	$Pb^{208}(C^{12}H_3)_2(C^{13}H_3)$

TABLE 2.4

RELATIVE ISOTOPIC ABUNDANCES FROM THE $Pb(CH_3)_3^+$ SPECTROGRAM

Mass number	Relative intensity	Lead isotope	Relative abundance, %
248	0.01 ± 0.005		
249	1.51 ± 0.005	204	1.569 ± 0.005
250	0.23 ± 0.01		
251	21.26 ± 0.02	206	21.97 ± 0.03
252	23.56 ± 0.02	207	23.41 ± 0.03
253	51.67 ± 0.03	208	53.04 ± 0.05
254	1.77 ± 0.005		

(absolute error is believed to be less than 1%)
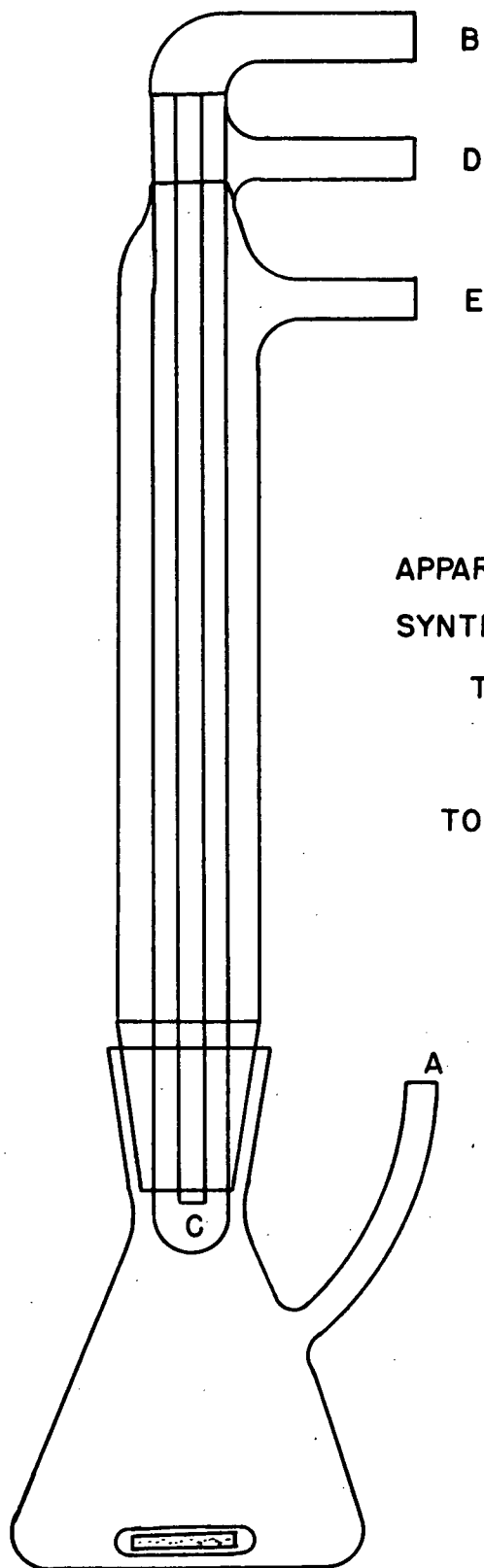
B

D

E

FIG. 2.3.

APPARATUS   FOR   THE

SYNTHESIS   OF   LEAD

TETRAMETHYL

TO   FOLLOW   P. 8

A

C

of an alkyl magnesium halide in ether, the reagent most often used being methyl magnesium bromide in diethyl ether.) The method used has been improved slightly over the years to give a better yield of lead tetramethyl, but the basis of their method is the same. The following is a typical technique.

Lead chloride is obtained from a sample (e.g. galena) by boiling it in hydrochloric acid, and after recrystallization the chloride is converted to lead iodide by reaction with potassium iodide. 200-500 mg. of lead iodide is thoroughly dried and placed in the apparatus shown in Fig. 2.3 through the side arm A. BCD is a simple water-cooled "finger" reflux condenser. All the air in the apparatus is displaced by passing dry oxygen-free nitrogen or argon by way of the lead-in E. Two cubic centimeters of ether are added to form a slurry and then an excess (5-10 ml.) of 0.5 mole-per-litre Grignard reagent is added and the mixture refluxed for one or two hours at about 35°C. After the reaction is complete water is added to consume the excess Grignard reagent and to wash out the water-soluble byproducts. The ether layer is then separated in a separatory funnel and the resulting ether solution dried with anhydrous calcium sulphate. In the past, separation of ether and lead tetramethyl has been effected by a crude distillation followed by a second distillation under vacuum in the mass spectrometer sample line.

CHAPTER 3

Gas Chromatography.

Etherington (1957) first attempted to separate lead tetramethyl from a mixture containing lead tetramethyl and ether using gas-liquid chromatography. This experiment, which forms the smaller part of Etherington's thesis, gave no positive result.

Before describing the details of the procedure developed by the writer, it is well to consider some general aspects of gas-liquid chromatography.

The main features of this method are shown in Fig. 3.1. 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 carrier gas. Because of their different physical properties, the constituents are transported through the column at different rates and emerge from it individually. The compositions of the effluent can be analysed quantitatively and qualitatively by a detector sensitive to some property of the vapours, usually the

FIG. 3. I.   DIAGRAM   OF   APPARATUS   FOR
GAS   CHROMATOGRAPHY
TO   FOLLOW   P. 10
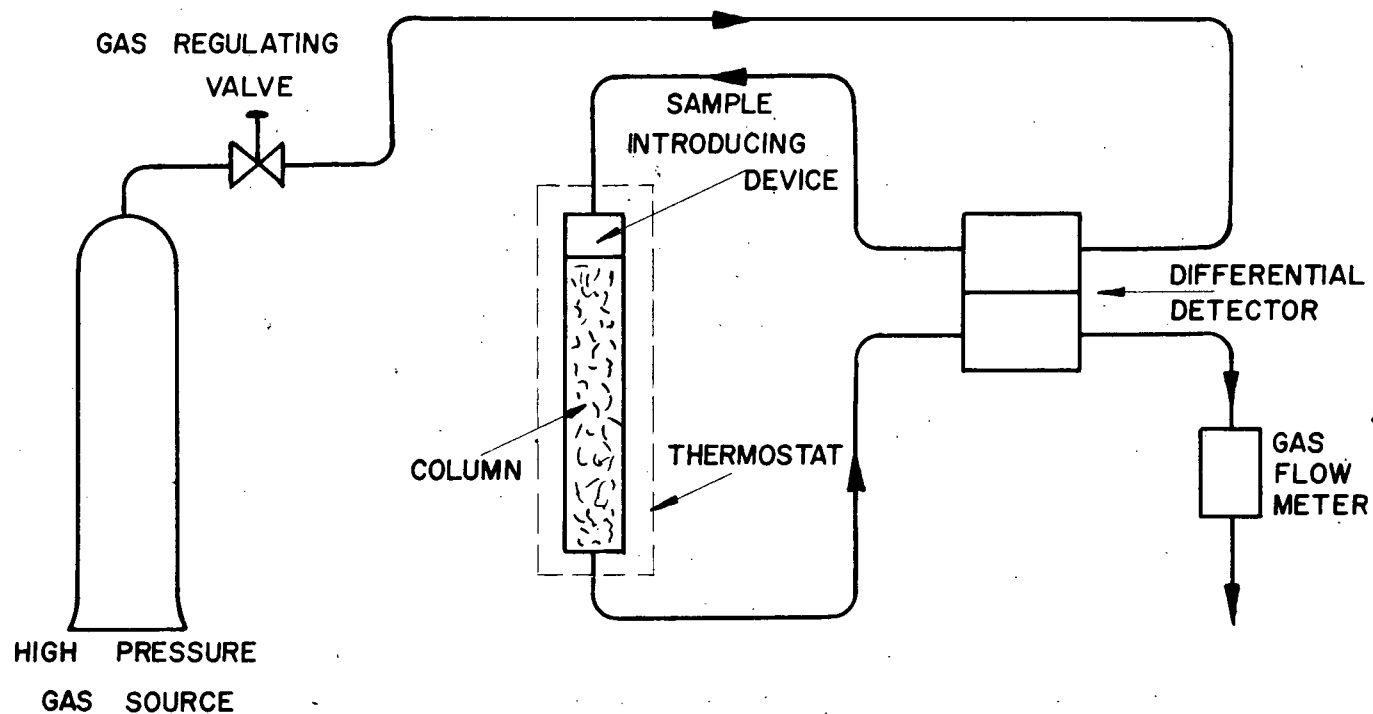
thermal conductivity.

There are various methods of analysing the effluent. Thermal conductivity, vapour-density balance, heat of adsorption are but a few. Thermal conductivity, however, is the most widely employed and is the method used by the writer. Fig. 3.2 (a) and (b) show the mechanical construction of the sensing instrument (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 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. (Type 9225 20 ohm, Gow-Mac Instrument Company, New Jersey.) Pure carrier gas was passed through channel #1, through the column and then through channel #2. The differences in resistance of the heated wires due to the presence of volatile components in the effluent were then recorded by means of the Wheatstone bridge arrangement shown in Fig. 3.2 (b) which gave an out of balance voltage recorded on a Brown 10 millivolt chart recorder. The particular mechanical arrangement shown in Fig. 3.2 (a) was chosen to minimize effects of flow fluctuations at the expense of a fast response.

The carrier gas should satisfy the following two re-

HERMETIC
SOLDERED
SEAL

+ −

CHANNEL # 2

SAMPLE

SAMPLE

CHANNEL # I

REFERENCE

REFERENCE

KATHAROMETER   BODY

MOUNTING   OF
SENSING
FILAMENTS

FIG. 3.2. (a)

PAIRS
R₁ − S₁
R₂ − S₂

ZERO
CONTROL

REFERENCE
GAS

SAMPLE
GAS

2 Ω

CURRENT
CONTROL
20 Ω

R₁

S₁

REC

S₂

5000 Ω

R₂

B +

SAMPLE

REFERENCE

B −

SCHEMATIC   4 FILAMENT   BRIDGE
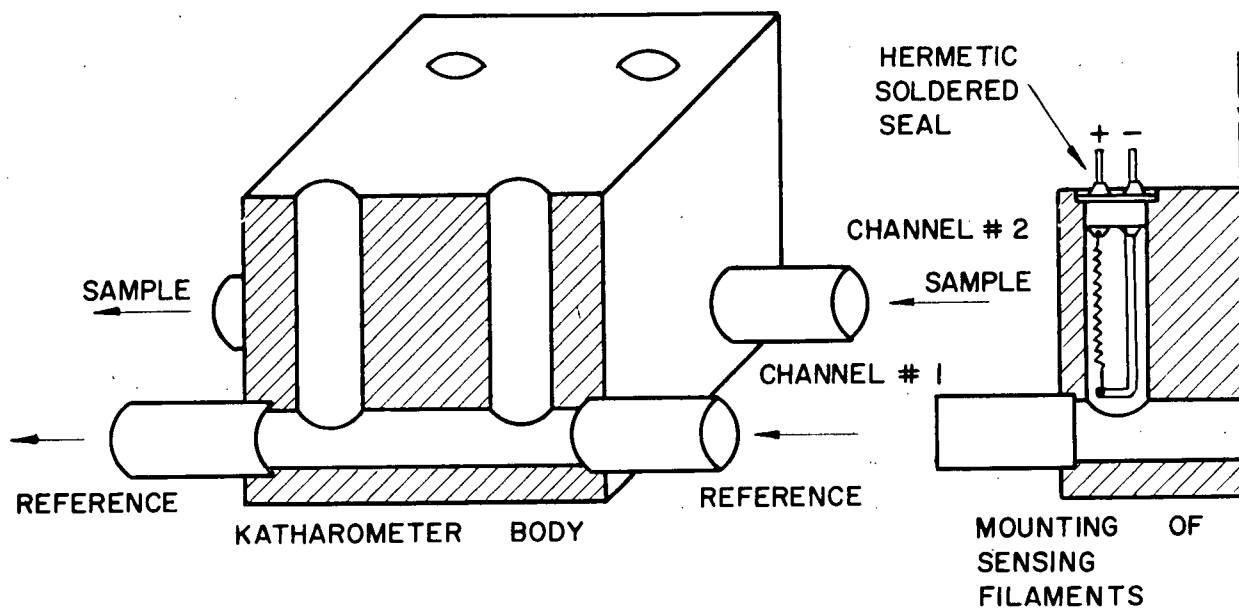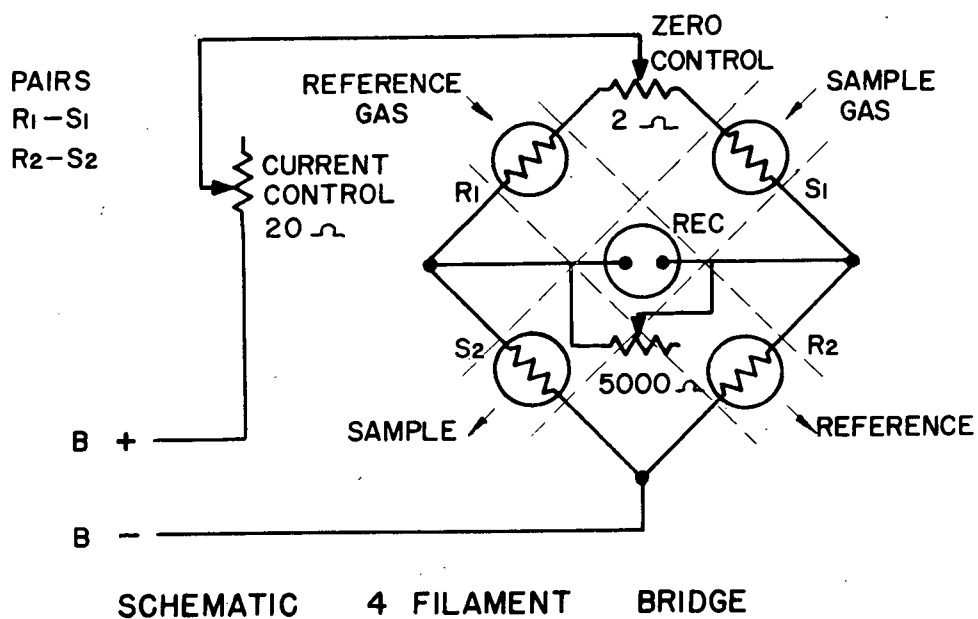
FIG. 3.2. (b)

quirements.

 (1) It should be inert.

 (2) Its thermal conductivity should be either somewhat greater or less than that for the vapours to be detected.

The above requirements are satisfied by a number of gases, the most readily available being hydrogen, helium and nitrogen. The thermal conductivities of the above relative to air are 7.10, 5.53 and 0.996. Hydrogen however is not recommended for safety reasons and helium is rather expensive for routine work where nitrogen will do. Although the sensitivities with nitrogen are much smaller than with either hydrogen or helium, they were ample for this problem.

Columns are usually constructed of pyrex or copper tubing. The internal diameter of such columns usually lies between 4 and 8 millimeters and their lengths vary with application from 1 to 20 meters. Since the resolution or the separating power of a column is proportional to the number of theoretical plates, the resolution can be increased by increasing the length and is roughly proportional to the square root of the column length. An increase in column diameter results in a decrease in resolution owing to the decrease in sharpness and uniformity of the moving fronts of the component bands. However a column of greater diameter can be used for large samples since the capacity of a column is proportional to the square of the diameter.

The solid support must meet the following requirements.

    (1)   It must have a large surface area to provide the maximum number of theoretical plates.

    (2)   It must be inactive with respect to the components of any given sample.

    (3)   It must permit a reasonable rate of flow without an excessive pressure drop.

The materials which give the best results have so far been limited to diatomaceous earths and several kinds of firebrick. The best compromise between column resistance and surface area is obtained from a type C-22 firebrick with particle size ranging from 60 to 80 mesh. The narrow limits of the particle size are necessary to ensure uniformity of packing with the consequent sharp and undisturbed moving fronts in the column.

The stationary phase in gas-liquid chromatography is an entire field of study in itself. The choice of a suitable partition liquid is the most important factor in obtaining good results, since its chemical composition will greatly affect partition coefficients. Several criteria affecting the choice of the partition liquid can however be treated generally.

The stationary liquid chosen should be virtually non-volatile at the operating temperature, i.e. the temperature of the mean boiling point of the sample. A vapour pressure of 1 micron at this temperature is usually considered the maximum permissible value consistent with long column life.

To function properly, the stationary liquid must produce a differential partitioning of the components to be separated and must have a sufficient solvent power for the vapourised components. The latter requirement demands a certain structural resemblance between the mobile and the stationary phase, since then ideal solutions are more closely realised in the column.

Polarity of the stationary liquid can also play an important role in separation efficiency. Liquids with increasing polarity will create stronger attractive fields around the dissolved molecules of the volatile constituents and exert strong attractive forces causing considerable deviations in the order of elution.

Gas-liquid chromatography can be a very precise technique. For this to be so, the column and the detecting device are enclosed in a thermostat capable of being regulated to $\pm$ 1°C, the gas flow is adjusted by a precision gas regulating valve and the pressure at the inlet and outlet of the column is usually regulated. In this work the writer was interested in a qualitative rather than a quantitative study and so discarded many of the finer details.

The apparatus used is shown in Fig. 3.3. It embodies a high pressure nitrogen cylinder, a gas regulating valve, the column, kept at an approximately constant temperature in a water bath in a dewar flask, the thermal conductivity sensing device previously described, a flow meter and a collecting arrangement.

FIG. 3.3.   EXPERIMENTAL   APPARATUS

TO   FOLLOW   P. 14
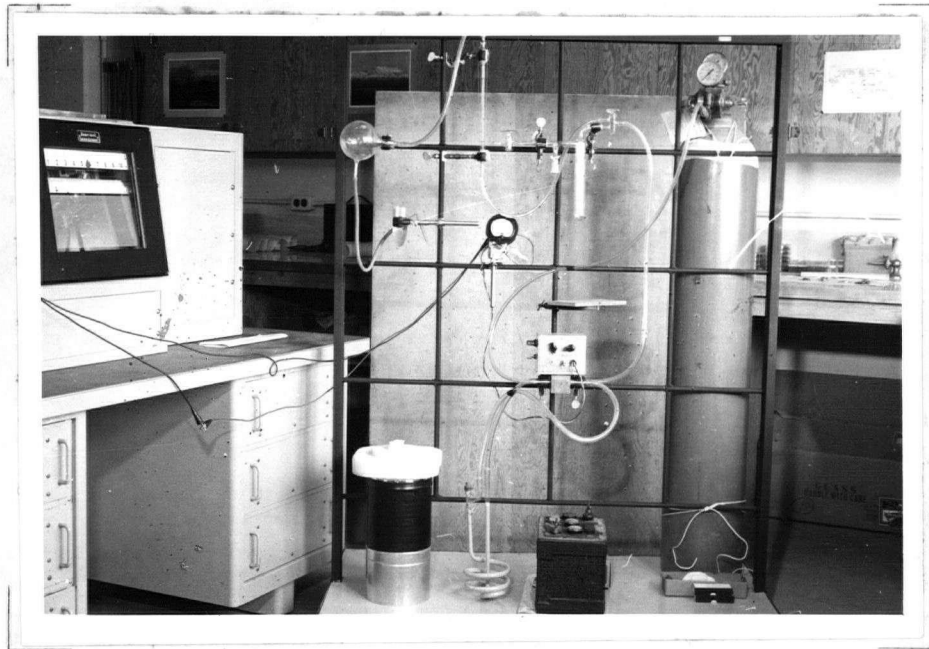
COLLECTING
ARRANGEMENT
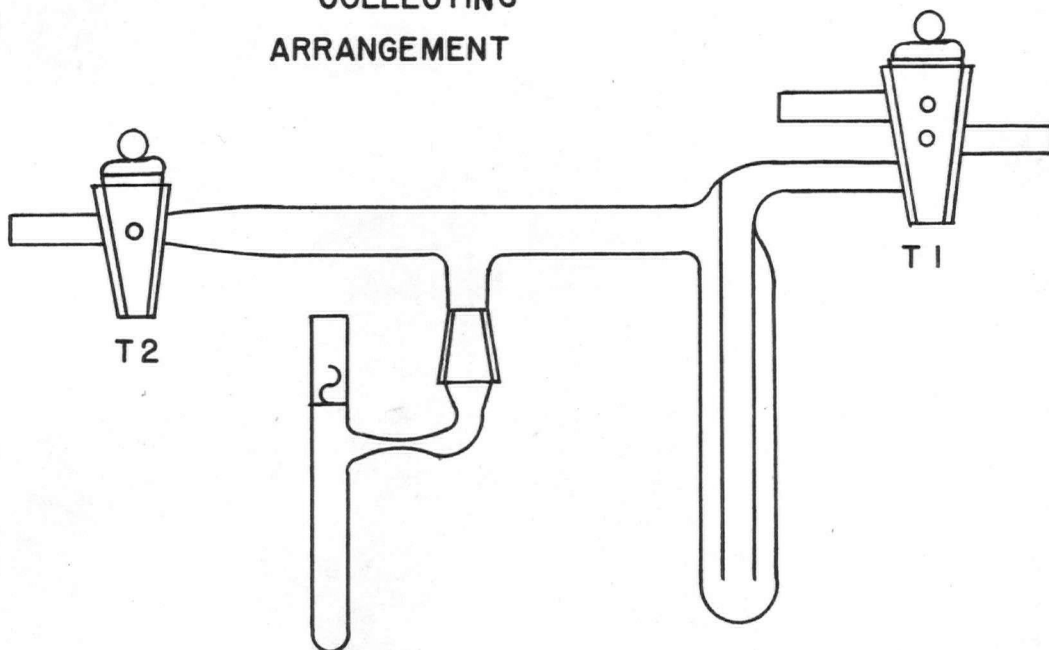
The immediate purpose of this work was to investigate
in general the use of gas-liquid chromatography in the
separation of contaminants from lead tetramethyl and to
purify samples prepared by the method described in Chapter 2.
With this purpose in mind, the writer first constructed a
4 mm. internal diameter, 50 cm. long, U shaped pyrex column.
The solid support used was a type C-22 crushed firebrick,
particle size 40-100 mesh. A. Keulemans (1957) lists the
principle types of stationary liquids used in gas-liquid
chromatography and their applications to various problems.
It appears that organic esters, i.e. esters of an aromatic
carboxylic acid and an aliphatic alcohol make stationary
liquids of very general applicability. (Some of them are
also used as diffusion pump oils, e.g. Octoils.) Keule-
mans summarises their properties in the following manner.

"The esters derived from aromatic acids, in particular,
usually show no pronounced selectivity over a wide range
of compound types, since they contain phenyl, aliphatic
and polar groups. They separate many classes of solutes
roughly according to volatility and can be employed, if
pure, for long periods up to 140°C."

In view of these considerations, the stationary liquid
chosen was dinonyl phthalate, a member of the phthalate
group or organic esters.

The ratio of stationary liquid to solid support was
chosen to be 30:100 parts by weight. If the proportion of

FIG 3.4. SEPARATION OF ETHER AND ACETONE
COLUMN #1
TO FOLLOW P. 15
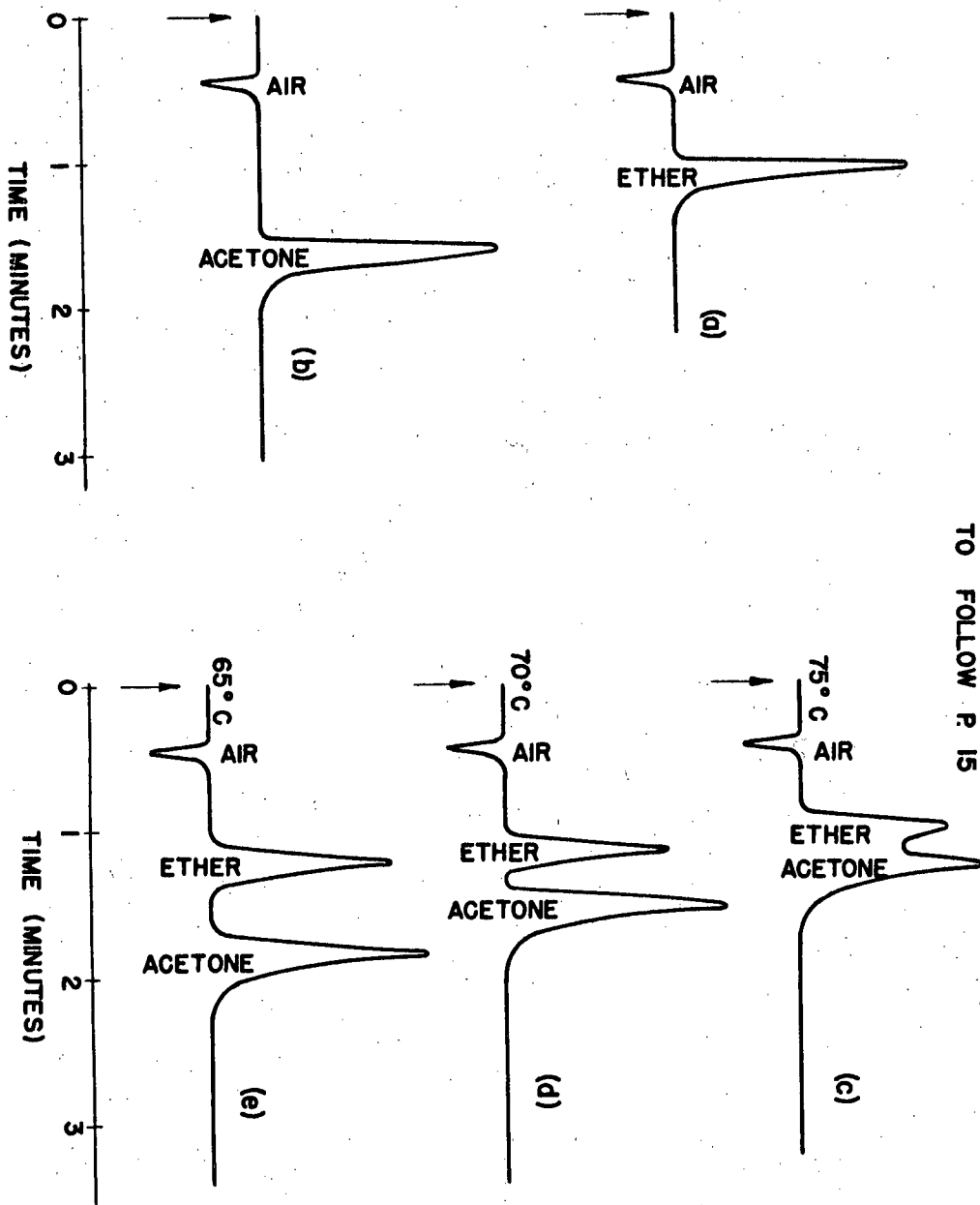
liquid is large, diffusive phenomena tend to impair the separation, while if the proportion is small, residual adsorptivity causes tailing of the elution peaks. The column material was prepared by dissolving the partitioning liquid in ether, mixing the dissolved liquid and the stationary support thoroughly and evaporating the ether at 50°C. The material was packed into the column and plugs of glass wool were placed at the ends. The liquid sample was introduced by means of a syringe. For this purpose a serum cap was used to close the front end of the column.

An obvious method of checking the separating efficiency of a column is by introducing a sample composed of two constituents of comparable volatilities and observing the separation. Ether and acetone serve this purpose well. Since theory shows that the efficiency of separation in a gas-liquid chromatographic column improves with reduction in sample size, throughout the experiments dealing with acetone and ether the sample introduced was in the form of the vapours of the constituents.

Fig. 3.4 shows the various chromatograms obtained with the first column. Curves (a) and (b) show the chromatograms for pure samples of ether and acetone respectively, at a temperature of 75°C and a flow rate of 50 ml./min. The first peak obtained in each case is due to air and is opposite in direction to the ether and acetone peaks since the thermal conductivity of air is higher than that of nitrogen, which in turn is higher than that of ether and
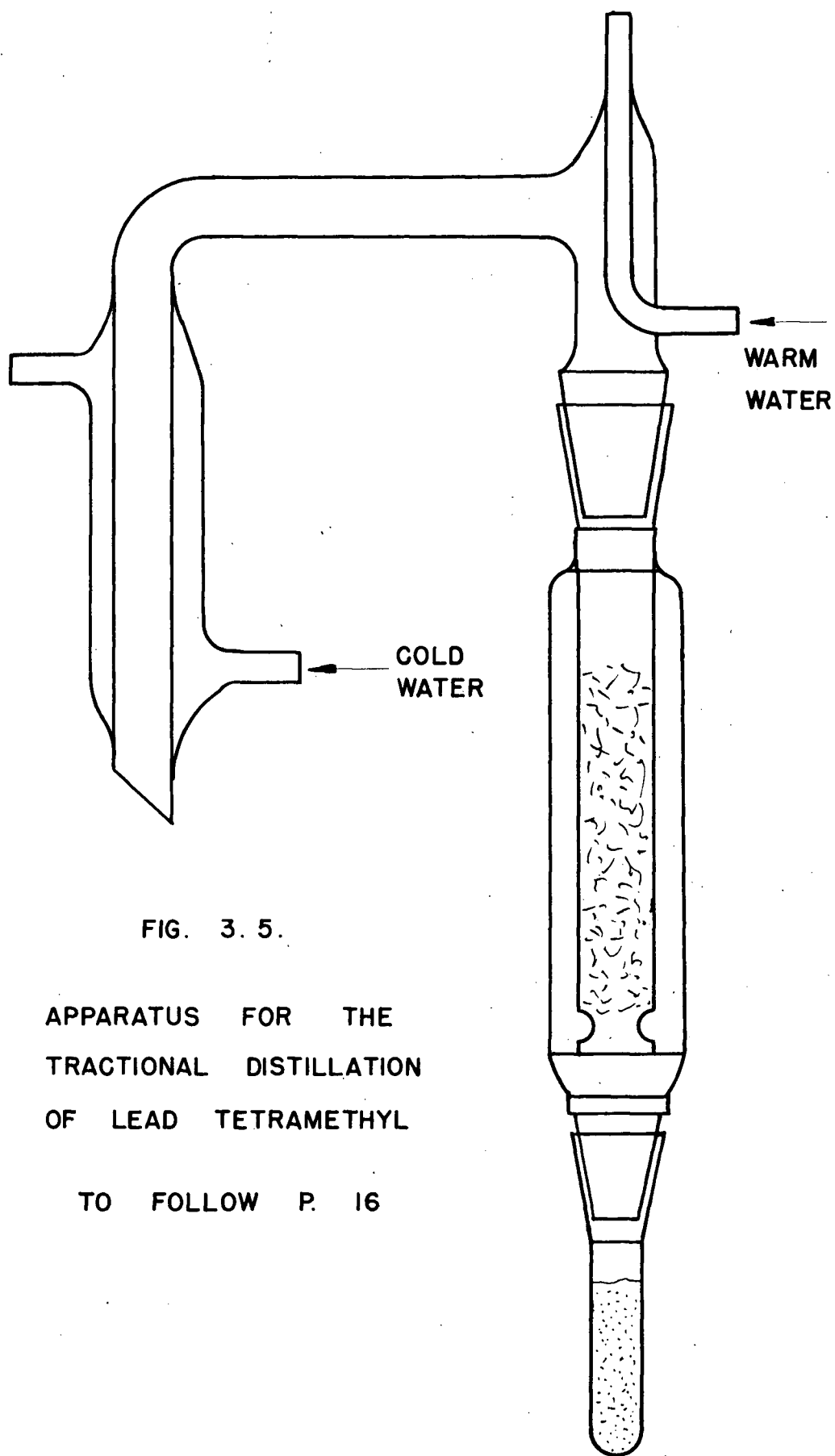
WARM
WATER

COLD
WATER

FIG. 3. 5.

APPARATUS FOR THE
TRACTIONAL DISTILLATION
OF LEAD TETRAMETHYL

TO FOLLOW P. 16

acetone. Curves (c), (d) and (e) show the separation of
ether and acetone at 75°C, 70°C and 65°C respectively
using a flow rate of 50 ml./min. in each case. Since the
range of volatilities of interest in the writer's case
was far larger than the one employed in the above experi-
ments, these results indicate that the separating ef-
ficiency of even a short column was sufficient for small
samples, especially if the temperature was kept close to
the median boiling point of the sample.

The writer next attempted to apply this method to
the purification of lead tetramethyl obtained by the
procedure described in Chapter 2.

The solution containing lead tetramethyl and ether
was fractionally distilled down to 1/4 cc. in the appa-
ratus shown in Fig. 3.5 which was designed with the help
of Prof. J.S. Forsyth. In such a fractionating column,
the vapour of the solution to be separated is passed
through the column and brought into contact with part
of the condensate which flows down the column. The less
volatile components of the ascending vapour are condensed,
while the more volatile components are boiled out of the
descending liquid phase. The distillation through the
column is thus equivalent to a number of successive
simple distillations. The efficiency of separation of a
fractionating column increases as the amount of vapour
condensed at the top of the column and returned as reflux,
increases. In the writer's case, the reflux ratio was

FIG 3.6. SEPARATION OF LEADTETRAMETHYL
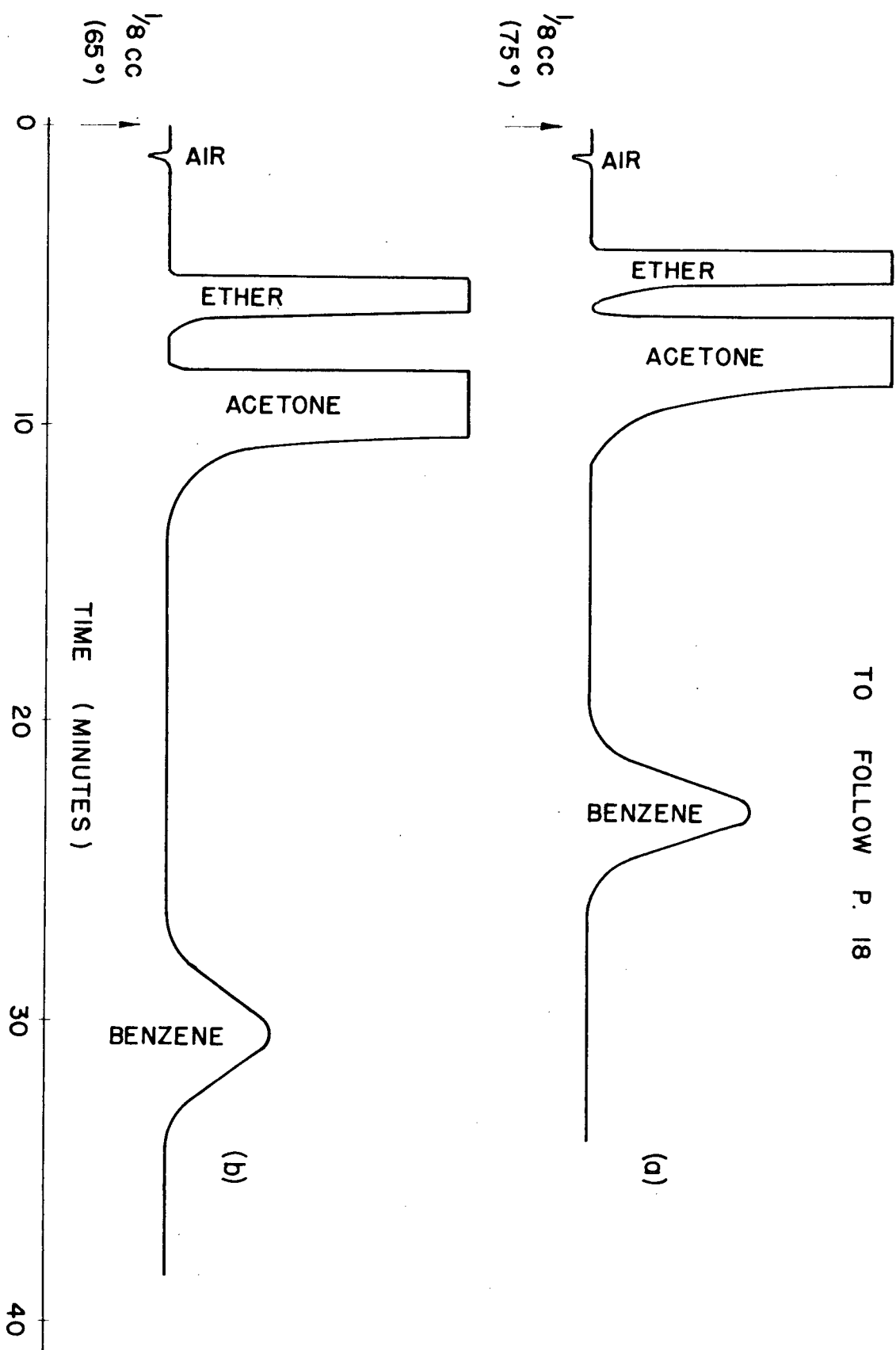COLUMN # I
TO FOLLOW P. 17
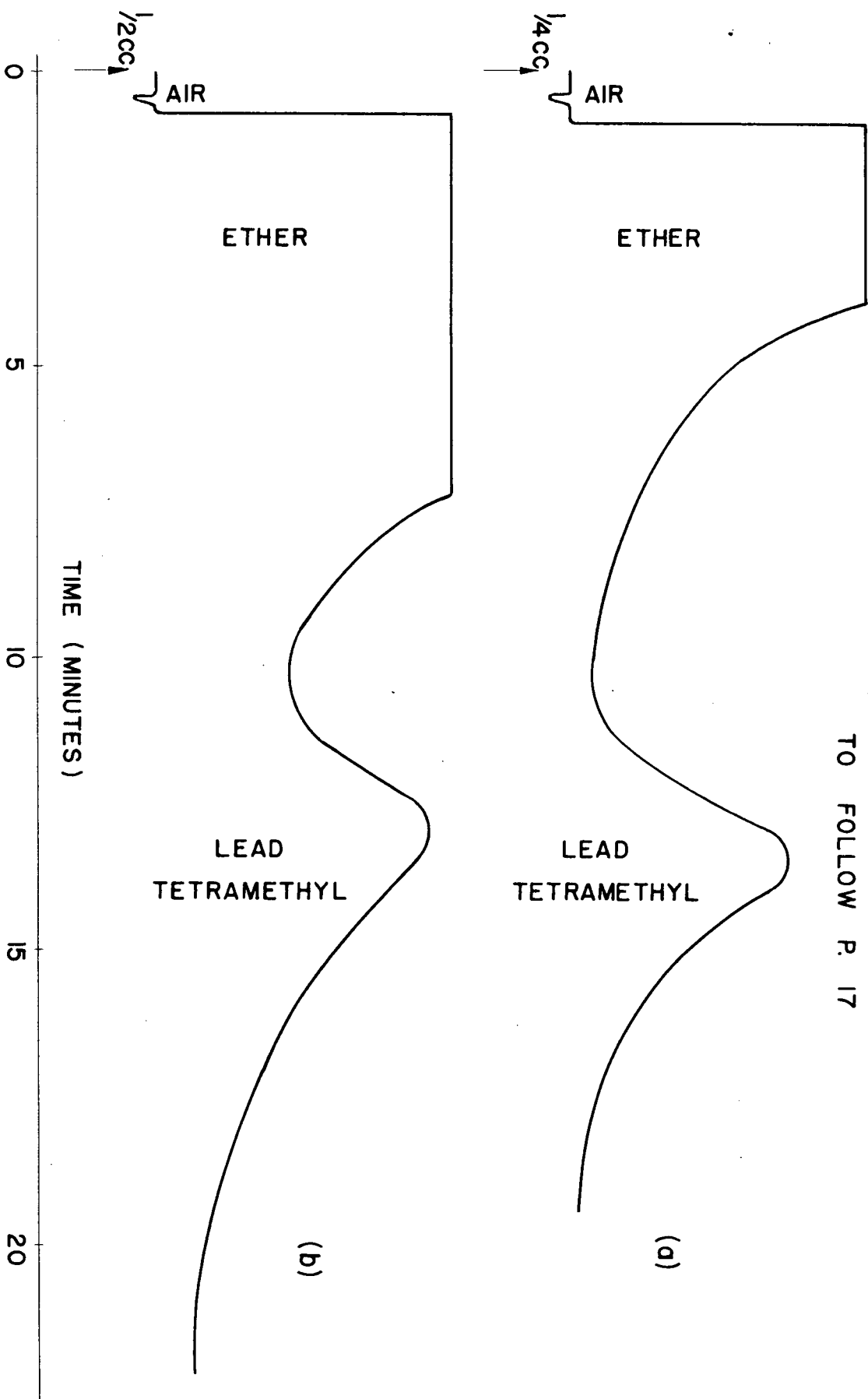
1 : 1. The purpose of the packing shown in Fig. 3.5, which was composed of small glass helices, was to provide good contact between the vapour and liquid phases in the column.

The distilled mixture was introduced into the column with a syringe and the lead tetramethyl was collected for analysis in the mass spectrometer. The method of collection was as follows. The dual stop-cock T_1, shown in Fig. 3.3, was set to allow the vapours emerging from the gas-chromatographic column to bypass the collecting apparatus and escape to the atmosphere via a dilute nitric acid bubbler. When the katharometer began to indicate the lead tetramethyl peak, stop-cock T_2 was opened and T_1 was turned to allow the lead tetramethyl to enter the collecting arrangement which consisted of a liquid air trap and a sample storage tube. At the end of the lead tetramethyl peak, as shown by the sensing device, T_1 was closed, the carrier gas was pumped from the collecting apparatus with the aid of a rotary vacuum pump and the apparatus was isolated by closing T_2. The dewar flask containing liquid air was then transferred to the sample storage tube into which the lead tetramethyl condensed. The sample storage tube consisted of a break-seal tube for long storage, or a tube terminated with a stop-cock for convenient handling for immediate use.

Fig. 3.6 curve (a) shows the chromatogram obtained. The separation was not complete due largely to the long ether tail. This tailing was probably due to two reasons. Firstly, the sample was not introduced as a "plug" at the

FIG 3.7. SEPARATION OF ETHER, ACETONE AND BENZENE

COLUMN # 2

TO FOLLOW P. 18

front end of the column, owing to the length of tubing be-
tween the serum cap and the layer of column material, re-
sulting in "exponential" flow and secondly the sample size
was very large for the column. Curve (b) shows the sepa-
ration obtained for a sample size of $\frac{1}{2}$ cc. which has de-
teriorated considerably with the large increase in sample
size.

Owing to the inherent inefficiency of the distillation
process and the incomplete separations obtained with the
50 cm. column, the writer constructed a column with a higher
sample capacity and higher separating power. As mentioned
previously, the first of these two factors can be attained
by an increase in column diameter, while the second factor
can be attained by an increase in column length. A new
column was therefore constructed using 1 cm. internal
diameter pyrex tubing wound into a $1\frac{1}{2}$ meter helix as shown
in Fig. 3.3. The column material was prepared as before
except that a solid support of a more uniform particle
size, ranging from 60 to 80 mesh, was used. Preliminary
experiments were performed using ether, acetone and benzene
in amounts 25%, 70% and 5% respectively. The sample size
was 1/8 cc. in each case at a flow rate of 50 ml./min.
Fig. 3.7 shows the chromatograms obtained. The separation
attained between benzene and ether was complete and could
be further increased by decreasing the temperature as
shown in curve (b). Since the boiling point of lead tetra-
methyl is approximately twice that of benzene and since the

FIG 3.8.   SEPARATION   OF   LEAD TETRAMETHYL
COLUMN   # 2
TO   FOLLOW   P. 19
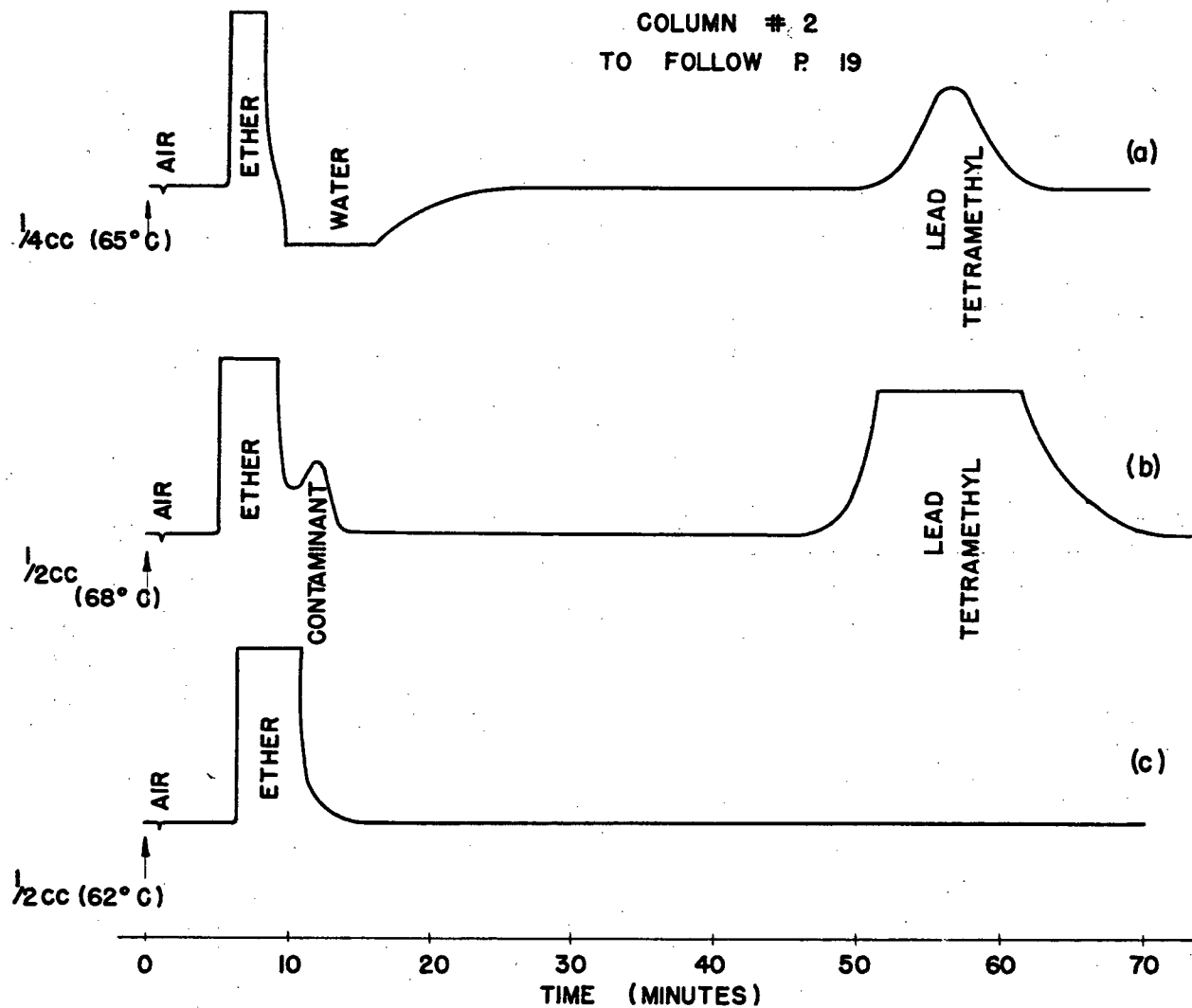
column separates roughly according to boiling point, the re-
sults would indicate that the new column satisfies the re-
quirements. The column was therefore applied to the problem
of separating lead tetramethyl from the unwanted constituents.

Before introduction into the column, a particular sample
was distilled down to approximately ½ cc. to avoid the possi-
bility of column saturation.

Before commencing each run, the temperature of the water
in the dewar flask was raised to approximately 95°C and
nitrogen was passed through the column to drive out any
vapours which may have remained in the column material.

Typical results obtained are shown in Fig. 3.8. Nitro-
gen at a flow rate of 50 ml./min. was used as the carrier
gas in each of the runs. Only two factors were altered
from run to run, the temperature and sample size as shown
on the curves .

Curve (a) shows the separation obtained when water
was present in the sample. The long tailing following the
water peak was due to the fact that few stationary liquids
are compatible with it and it is often adsorbed to a certain
extent by the solid support.

Curve (b) shows the separation obtained when water was
removed completely prior to the separation. A contaminant
peak, probably masked by the water peak in curve (a),
follows the ether peak. This contaminant could be mercury
dimethyl which is often observed in the mass spectrometer.

Curve (c) shows the chromatogram of the distillate

TYPICAL   Pb $(CH_3)_3$ SPECTROGRAM   OBTAINED
TO   FOLLOW   P. 20

2

5

4

4

2

2
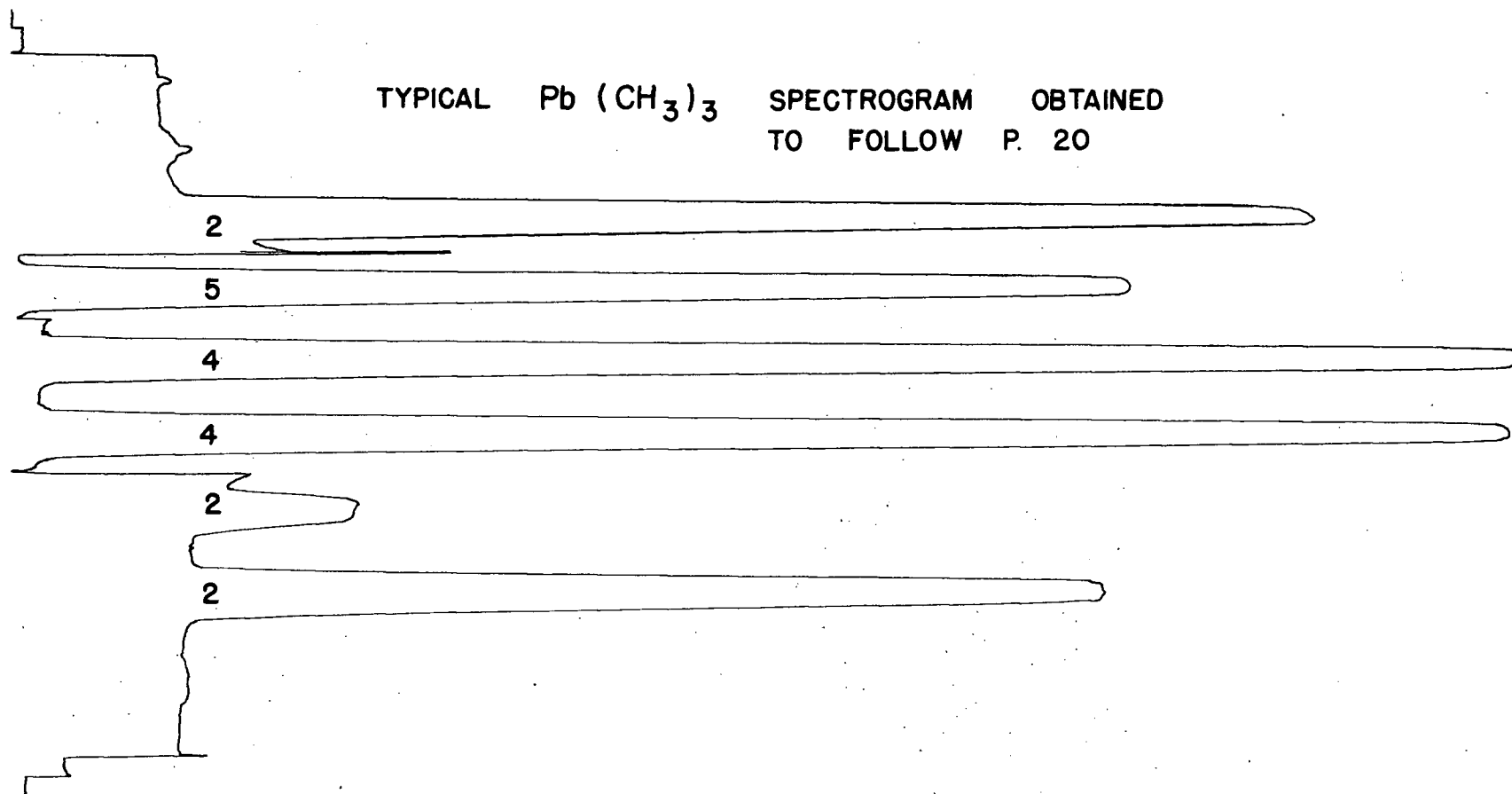
obtained from the initial separation. No lead tetramethyl peak is present, showing that the distillation as used is nearly 100 percent efficient.

The time required for the complete separation was of the order of 70 minutes, but this time can be greatly shortened, if desired, by increasing the temperature as indicated by the curves in Fig. 3.7.

The technique developed was applied to the analyses of six samples from the conformable lead deposits at Broken Hill, New South Wales, Australia and one sample from the conformable lead deposits at Mount Isa, Queensland, Australia with results being published by Kollar, Russell and Ulrych (in press). Using a mass spectrometer technique developed by F. Kollar a precision ten times better than previously possible was obtained. This has made it possible to distinguish an age difference of 10 million years between formations 1500 million years old, a precision that has never been possible before by any radioactive age determination method.

Fig. 3.9 shows the $Pb(CH_3)_3^+$ mass spectrum of a sample prepared and purified as described.

CHAPTER 4

Free Radicals.

It was first shown in an experiment by Paneth and
Hofeditz that free methyl radicals could be detected by
their removal of lead mirrors. In this experiment, methyl
free radicals were obtained from the thermal decomposition
of lead tetramethyl, and the reaction was assumed to be:

$$Pb(CH_3)_4 = Pb + 4CH_3$$
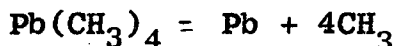
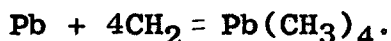The free methyl radicals thus formed reacted with the lead
mirror to form lead tetramethyl by

$$Pb + 4CH_2 = Pb(CH_3)_4.$$

The latter reaction is the basis of the method of
producing lead tetramethyl which the writer hopes to
employ in conjunction with his Ph.D. research programme.
The feasability of this method has been well demonstrated
by A. Surkan (1956) who, however, was discouraged from
developing it into a useful technique owing to the
presence of contaminants in the critical mass ranges.

The dissociation of a compound with the resulting
production of free radicals may be performed in one of
several ways, the chief methods being thermal (pyrolyses),
photolyses and electric discharges.

Dissociation occurs when the thermal energies of
the molecules exceed their bond dissociation energy. This
method has been widely used since 1933 when Leermakers

showed that free methyl radicals could easily be obtained in quantity by heating azomethane to 400°C. In 1934, F.O. Rice et al. showed that at temperatures of 800°C or greater, the pyrolyses of the vapours of a whole range of stable organic compounds, such as paraffin hydrocarbons, ether, alcohols, aldehydes, ketones and amines yield the simple alkyl radicals methyl and ethyl. The disadvantages of this method are the high temperatures necessary with the resulting experimental difficulties and the fact that investigations have shown that, in pyrolyses of organic molecules, free radical formation often compromises only a small proportion of the total reaction.

Between 1931 and 1934, Norrish et al., after detailed study of the photochemical decomposition of aldehydes and ketones, concluded that when acetone vapour is exposed to ultraviolet light, the initial reaction is the decomposition into free methyl radicals. Pearson in 1934 substantiated this conclusion by using Paneth's mirror technique. There is now abundant evidence that the photochemical decomposition of molecules of all types, in the liquid or gaseous phase, leads to the production of active free radicals.

Two fundamentally different types of electrical discharge occur. The silent or non-disruptive and the disruptive discharge. The former includes types such as the ozoniser, corona, electrodeless discharge. From investigations with a variety of substances there can be no

doubt that the silent discharge decomposes organic and inorganic compounds into atoms and radicals, but the situation is usually too complex to enable precise predictions to be made. The disruptive discharge, the arc and the spark, is much more violent, with the result that practically every possible atom or radical is produced. This makes the analysis of the results of such a discharge almost impossible. The main effects of these discharges are thermal in nature, corresponding to localised heating of the gas to a very high temperature.

Other methods exist, such as electrolysis, but for various reasons these do not lend themselves to the routine preparation of lead tetramethyl.

Surkan in 1956 attempted to produce lead tetramethyl by the reaction of lead with free radicals in sufficient quantity for use in a mass spectrometer. It is of interest here to summarise his methods and results.

Surkan experimented with two types of free radical forming mechanisms. High frequency discharge and thermal decomposition. The sources of free methyl radicals used were acetaldehyde, acetone, methyl alcohol, methane, ethane and propane. Of the two mechanisms used, Surkan found the high frequency discharge to be superior if used at low power to avoid impurities. By attack of standard lead mirrors he found that acetone and methyl alcohol gave the greatest yield of free methyl radicals. However, from the point of view of low impurities and high yield, methane

gave the best results.

Surkan produced sufficient lead tetramethyl to yield high intensity ion beams in the mass spectrometer from 500 μg. of lead, which is less by a factor of twenty than the amount necessary in the present method of preparing lead tetramethyl. A serious problem in Surkan's method was the contamination of the reaction products, making impossible the accurate determination of the isotope abundances.

Conclusions.

Two types of mass spectrometer are used for lead iso-
tope studies. Gas source and solid source instruments.
The former type has advantages which resulted in its choice
for use in this laboratory. Two problems arise when the
gas source instrument is used for lead isotope analyses.

The first problem concerns the sample size. The lead
to be analyses is introduced into the mass spectrometer in
the form of lead tetramethyl vapour. The present chemical
technique used in preparing lead tetramethyl necessitates
the use of a minimum of 8 mg. of lead. It would be highly
impractical to try and obtain lead in such quantities from
certain types of minerals, e.g. zircons, in which the lead
concentration is small.

The writer therefore investigated a new method of
producing lead tetramethyl from microgram quantities of
lead, a problem first studied by Surkan. Surkan, using
free methyl radicals produced by high frequency discharge
in propane, methane and acetone, obtained sufficient lead
tetramethyl for analysis in a mass spectrometer. A large
amount of contaminants were however obtained, some in the
mass range of interest, making any useful isotope measure-
ments impossible.

The writer's brief investigations into free radicals
would indicate that photolysis of acetone vapour is
capable of producing large quantities of free methyl
radicals with smaller amounts of contaminants than electri-

cal discharge and is more convenient a method than pyrolyses.

The experiments performed with gas-liquid chromato-
graphy show that lead tetramethyl can readily be separated
from any contaminants obtained. The writer hopes to develop
the free radical technique as part of his Ph.D. research.

The second problem concerns the purity of the lead
tetramethyl sample obtained by the usual technique described
in Chapter 2, in which the main contaminant is ether.
Distillation, if carried too far will result in loss of lead
tetramethyl. Other contaminants may be water, which can
usually be removed by careful chemistry, and such compounds
as mercury dimethyl or other byproducts of the reaction be-
tween the Grignard reagent and the somewhat impure lead
iodide obtained from the mineral.

Contaminants can have serious effects on the precision
of analysis. Ether, because it is a large proportion of the
sample and because of its high vapour pressure, raises the
pressure of the mass spectrometer vacuum system and causes
pressure scattering with the resulting tailing of the iso-
tope peaks. Other contaminants, if falling in the mass
range of interest, can drastically change the isotope ratios,
affecting particularly the abundance of lead-204.

The technique developed by the writer has overcome the
difficulties mentioned above. Analyses recently completed
in this laboratory by F. Kollar and others involved lead
samples from 200 square mile areas in Broken Hill, Australia
and Mount Isa, Australia. The isotope ratios in each

district are predicted to be identical (Stanton, Russell 1959). In attempting to verify this theory, Kollar obtained a 0.05% precision by using a specially constructed gas source mass spectrometer with a new technique involving the direct intercomparison of two samples. In order to do this, he required very pure samples of lead tetramethyl, since only then can conditions in the mass spectrometer be kept the same for both samples and the possibility of contamination be avoided.

Six samples from Broken Hill, New South Wales and one from Mount Isa, Queensland were analysed by the time this thesis was prepared. It was found that the Pb^{207}/Pb^{206} and Pb^{204}/Pb^{206} isotope ratios in each district were identical within 0.05%. Furthermore there was a 0.5% difference in the isotope ratios from the two localities separated by eight hundred miles. From these results it can be inferred that the leads from the two districts lie approximately on the same lead-uranium-thorium curves and that the Mount Isa lead is about 50 million years younger than the Broken Hill lead. The latter result is of great importance since the age difference is only 3% of the ages of the two deposits and represents a significant increase in the precision with which ages in this range can be compared by this or similar methods.

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