ProQuest Number: 10701116

ProQuest 10701116

A MOSSBAUER STUDY OF GAMMA-IRRADIATED

ORGANOTIN-STABILISED POLY(VINYLCHLORIDE)

by

JOHN UNWIN BSc

A Thesis submitted to the Council for National
Academic Awards in partial fulfilment of the
requirements for the Degree of Doctor of Philosophy

Sponsoring Establishment : Departments of Chemistry
and Applied Physics,
Sheffield City Polytechnic

Collaborating Establishment : Ministry of Agriculture,
Fisheries and Food
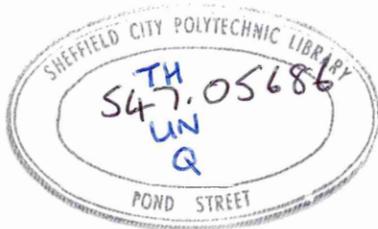
March 1986

ABSTRACT

A Mössbauer Study of Gamma-Irradiated Organotin-Stabilised Poly(vinylchloride)

by

John Unwin

^{119}Sn Mössbauer spectroscopy has been used to study the nuclear environment of three organotin stabilisers present in PVC, after exposure of the polymer to γ-irradiation up to a maximum dose of 200 kGy, in order to identify the tin-containing degradation products which could migrate into foodstuffs in contact with the polymer.

Chapter One of this thesis covers the aspects of the degradation and stabilisation of organotin-stabilised PVC which may influence the chemical nature of the tin-containing degradation products resulting from γ-irradiation of the polymer. Chapter Two contains a description of the theory of the Mössbauer effect and the instrumentation and computational methods for recording and processing Mössbauer data. Chapter Three is concerned with the effect of γ-irradiation, at doses in excess of food irradiation applications, in order to identify the terminal tin-containing degradation products of the stabilisers. In Chapter Four, evidence for the progressive degradation of organotin stabilisers upon increasing irradiation exposure is presented and intermediate degradation products are proposed. A mechanism for the degradation of stabilisers is suggested. In Chapter Five, evidence for dealkylated tin-containing degradation products in irradiated organotin-stabilised PVC is presented. Chapter Six involves the application of the Debye model of solids to variable temperature Mössbauer data for two organotin stabiliser degradation products, dibutyltin dichloride and stannic chloride, in PVC. A significant change in recoilless fraction is shown to occur when these compounds are dispersed in PVC compared with those of the pure compounds. This is attributed to changes in coordination number of the tin atom upon dispersion in PVC, and has a significant effect upon the relative sensitivity of the technique to the degradation products. Chapter Seven contains a comparison of the degradation processes occurring in thermal and γ-irradiation degradation of organotin-stabilised PVC. It is shown that degradation of the stabiliser during γ-irradation is much more severe. In Chapter Eight, an appraisal of the key experimental results and their implications for the γ-irradiation sterilisation of polymer-packaged foodstuffs is presented.

C O N T E N T S

Page

CHAPTER 1 :   ASPECTS OF THE STABILITY OF POLY(VINYLCHLORIDE)

1.1 INTRODUCTION

The world's food requirements continue to grow, but in an environment of scarce resources and limitations on methods of food production. In addition, the problems of food storage and processing make it necessary to search for effective alternative methods of food preservation, particularly where existing methods are costly because of the energy requirements, for example in remote areas of third world countries. It is reasonable to consider as an alternative, the use of ionising radiation for food storage and preservation provided that it does not adversely affect the wholesomeness of the food.

The use of ionising radiation as a process for food preservation has been under study for over thirty years. In the United Kingdom, the Food (Control of Irradiation) Regulations 1967 forbid the sale of irradiated food for human consumption other than for patients needing sterile diets as part of their treatment. However, the position is currently being reviewed by the Advisory Committee on Irradiated and Novel Foods in the light of the 1981 Report of the Joint Food and Agriculture Organisation/ International Atomic Energy Agency / World Health Organisation Expert Committee on Irradiated Food,[1] which concluded that irradiation of any food commodity up to an overall dose of 10 kGy presents no toxicological hazard.

1.2 FOOD IRRADIATION AND FOOD PACKAGING

Exposing food in sealed containers to ionising radiation at absorbed doses high enough (25 - 70 kGy) can kill all organisms of food spoilage and public health significance and impart commercial sterility.[2] It will, for example, kill microorganisms in foods that are contained in hermetically-sealed packages or in the frozen state. Moreover, the treatment can be carried out at room temperature without raising the temperature of the product. This may be an advantage if the physical properties of the packaged food are sensitive to temperature changes.

The absorbed radiation may, however, cause changes in the food and the packaging. The wholesomeness of irradiated food has been extensively investigated by many workers;[3,4] however, there is little published work on the packaging aspects of radiation sterilisation[5] and a recent survey has indicated the lack of information on the effects of gamma-irradiation on food packaging polymers.[6] Flexible and rigid polymers, as supplied to the food packaging industry, are multicomponent mixtures containing intentional and unintentional additives, e.g., antioxidants, plasticisers, lubricants, catalyst residues and monomers. Many of the additives will have been consumed, in part or in full, during manufacture of the polymer and converted into unknown degradation products. These polymers would then be irradiated in contact with the food under external

aerobic conditions and left in contact with the food
for extended periods of time where migration of additives
and their residues could occur. Hence contamination of
food by small amounts of a large variety of chemicals
is inevitable. The problems posed by the possible
regulation of radiation sterilisation for polymer-
packaged foodstuffs are therefore complex.

A survey carried out in 1962[7] on the effects of radiation
on packaging materials in the dose range 10 - 60 kGy
concluded that most food packaging materials performed
satisfactorily, and at absorbed doses of less than
10 kGys, only minor chemical changes were induced.
Specific investigations[8] into the effect of 25 kGy doses
on the migration of additives into food simulants
showed variable behaviour, depending on the polymer and
the additive, but it was established that changes do
occur in migration behaviour of such additives.

In 1964, the U.S. Food and Drug Administration (F.D.A.)
published a regulation of polymers for food contact
which could be irradiated up to 10 kGy. This list was
updated in 1982 and permitted polymers with general
classes of additives were given.[9] A paper produced by
the U.S. Army Natick Laboratory in 1972[10] concluded
that the gamma-irradiation of nine plastic films produced
extractable material which was identical to that extracted
from unirradiated polymers. The amount extractable was
dependent upon polymer and dose, in some cases being

greater and sometimes less after irradiation. The techniques used in this study and most other investigations are likely to have missed trace levels of contaminants and given little information on the chemical structures of the additive degradation products.

Clearly, if irradiation in any form is to be used on packaged food, it is essential to know the effect of irradiation on the package, the likelihood of interaction between the food and package during irradiation, and the properties of the irradiated food, in order to avoid objectionable changes in the food or package.

1.3 DEGRADATION AND STABILISATION OF POLY(VINYLCHLORIDE)

A recent survey[11] has shown that in Europe, PVC accounts for greater than thirty per cent of polymer products used in contact with foodstuffs due to the high clarity of the polymer and its resistance to most oils and fats. This makes it very useful for packaging of food and drink and long-term preservation of foodstuffs.[12,13]

The extensive applications of PVC have evolved despite one potentially serious drawback; the polymer is readily degraded by heat[14-18] at temperatures above 100-120°C, and upon exposure to short wavelength light,[19-23] undergoing a spontaneous dehydrochlorination reaction[24] (reaction (1)):

$$-\left[CH_2\underset{\underset{Cl}{|}}{CH}\right]_n \longrightarrow \left[CH=CH\right]_n + nHCl \qquad (1)$$
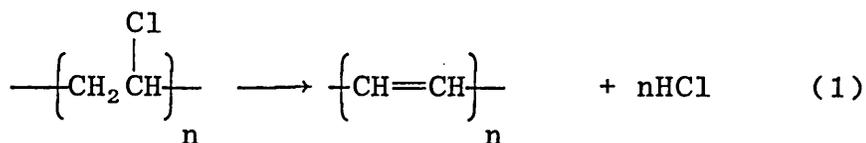
The above reaction is often described as a 'zipper-like' process and results in a system of conjugated double bonds in the polymer. As the degree of conjugation increases, the PVC blackens, after as little as 0.1% of the polymer has decomposed.[25] The hydrogen chloride evolved during this process is believed to have an auto-catalytic effect on the thermal degradation.[26,27]

The following structural irregularities have been discussed as possible initiation sites for dehydrochlorination:[26]

(a) chain end groups

(b) intra-chain branches

(c) random unsaturation involving allylic chlorine atoms; and

(d) oxidation structures, containing peroxide links.

Of these, the presence of random double bonds and allylic chlorine atoms are thought to contribute to the dehydrochlorination process to the greatest extent. It has been shown that degradation is more rapid in the presence of oxygen.[28] This may be due to the formation of hydroperoxides, which are thermally unstable, and are broken down to give carbonyl-substituted allylic groups (reaction (2)). These are considered to lead to even greater thermal instability:[29]

$$\sim CH-CH=CH-CH\sim \quad \xrightarrow{-H_2O} \quad \sim C-CH=CH-CH\sim \qquad (2)$$
$$\underset{\underset{OH}{\overset{|}{O}}}{|} \qquad \underset{Cl}{|} \qquad \qquad \underset{O}{\parallel} \qquad \qquad \underset{Cl}{|}$$
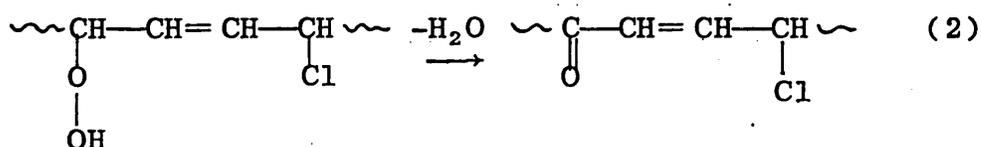
It has been recognised that during the photodegradation of PVC, dehydrochlorination occurs with concomitant discolouration of the polymer due to polyene formation and subsequent chain rupture and cross-linking.[30-37] In the photodegradation of PVC, the initiation step is one of the most important processes and controls the successive degradation. It has been stated that foreign materials and structural irregularities arising during the polymerisation or processing are possible initiating chromophores because PVC is structurally not expected to absorb light of wavelength above 220 nm.[30,38] The photodegradation mechanism, especially the initiation step, is not fully understood and different mechanisms have been reported.

Kwei[31,32] reported that the initial dissociation of chlorine atoms with ultraviolet light was correlated with the presence of ozone, and β-chloroketones were formed in the photooxidation of PVC. Scott and Tahan[33] suggested that during the photo-oxidative degradation of PVC, carboxyl groups were produced via photolysis of the intermediate chloroketones formed by abstraction of the methylene hydrogen. Ranby et al[34] reported that the most probable chromophores present in PVC are double bonds distributed at random together with a small number of carbonyl groups (1 carbonyl group for 100-1000 monomers) and the latter could be responsible for the photo-initiation process. Decker and Balandier[36] concluded that, primarily, labile allylic carbon-chlorine bonds are cleaved to produce α-chloroperoxy radicals which are

non-terminating and yield alkoxy-radicals that propagate
or decompose by β-scission of C-C and C-Cl bonds.

The result of the above degradation processes not only
produces colouration of the PVC but leads to
embrittlement and loss of tensile strength of the
polymer.[39] Fortunately it has been found that the
incorporation of certain additives into the PVC matrix
stabilises the polymer against the degradation processes.
Four main types of metallic stabilisers are generally
used and these are based upon the following:[40]

1. Organotin compounds

2. Lead compounds

3. Barium-cadmium soaps

4. Calcium-zinc soaps.

Of these classes, the organotin compounds are probably
the most effective stabilisers available, being
unequalled in their degree of stabilisation in both the
long and the short term, and in the clarity which they
produce in PVC products.

From the degradation processes just described for PVC,
it is apparent that for a compound to be an effective
PVC stabiliser, it should a) neutralise the liberated
hydrogen chloride, b) remove the developing unsaturation
before conjugated sequences are formed, c) replace labile
allylic chlorine sites in the polymer with more stable
groups, and d) remove peroxides. With regard to the
stabiliser itself, it should be innocuous, non-migrating

non-toxic, odourless and should not impair the clarity or other properties of the PVC.[39]

Most organotin stabilisers may be represented by the formula R_2SnX_2, where R is usually an alkyl-group and X is usually an ester of maleic acid or thioglycollic acid. Organotin stabilisers therefore, can be divided into two groups; those containing a tin-sulphur bond, which in general are the most effective heat stabilisers, and those containing a tin-oxygen bond which are usually used when good light stability is required. Table 1.1 lists the most common organotin PVC stabilisers.

The mode of action of organotin stabilisers probably involves a combination of effects, the most important of which are:[39]

1. inhibition of the dehydrochlorination reaction by exchange of their anionic X-groups with reactive allylic chlorine atom sites in the polymer,

2. removal of hydrogen chloride which is liberated, and which has an autocatalytic effect on the degradation rate, by reaction with the stabiliser to form organotin chlorides, R_2SnClX and R_2SnCl_2,[41]

3. for organotin mercaptides, which have an anti-oxidant action, destruction of the hydroperoxide groups which may be formed in the polymer and act as initiation sites for thermal degradation,[42] and

Table 1.1 Common Organotin PVC Stabilisers

Stabilisers	R
$R_2Sn(SCH_2CO.O^iOct)_2$	Me, Bu, Oct, BuOCO.CH_2CH_2
$RSn(SCH_2CO.O^iOct)_3$ [a]	Me, Bu, Oct, BuOCO.CH_2CH_2
$R_2Sn(SC_{11}H_{23})_2$	Me, Bu
$(RSnS_{1.5})_4$	Bu
$R_2Sn(OCO.C_{11}H_{23})_2$	Bu
$\{R_2Sn(OCO.CHCHCO.O)\}_n$	Me, Bu, Oct
$R_2Sn(OCO.CHCHCO.OR')_2$ [b]	Me, Bu, Oct

a   Used with corresponding dialkyl compound

b   R' = Me, Bu, ^iOct

(Data obtained from A. G. Davis and P. J. Smith, in

'Comprehensive Organometallic Chemistry', Ed.

G. Wilkinson, Pergamon Press, Oxford, 1982, Vol 2, p 519.)

4.   the addition of free mercaptans, produced from the
reaction of hydrogen chloride with an organotin
mercaptide stabiliser, to double bonds thereby
shortening the polyene sequence.[43]

The influence of the alkyl-group, R, on the effectiveness
of organotin stabilisers, using a series of di-n-
alkyltinbis(isooctylthioglycollates), has shown that
there is little to choose between the compounds from
methyl to octyl.[41] Aryl and certain substituted alkyltin
derivatives show reduced activity as stabilisers which
has been attributed to their higher susceptibility to
tin-carbon bond cleavage by hydrogen chloride.[41]
Therefore only derivatives of methyl, butyl and octyl-
tins have been developed as the main stabiliser types.

1.4   THE MECHANISM OF STABILISATION OF ORGANOTIN STABILISERS

The mode of action of organotin stabilisers has been
discussed in numerous books and reviews.[44-60] However,
the mechanism of stabilisation is not fully understood
despite much work carried out in this area.[61-69]

A detailed investigation carried out by Fry et al[46]
into the thermal stabilisation of PVC by compounds of
the type R_2SnX_2 showed that neither R-groups nor tin
atom were permanently attached to the polymer, but there
was evidence that the chlorine atoms of the polymer
were coordinated to the tin atom of the stabiliser. A
mechanism of stabilisation was suggested in which

X-groups were exchanged for the chlorine atoms to form the dialkylchlorotin ester, R_2SnClX, or dialkyltin dichloride:

$$R'Cl + R_2SnX_2 \longrightarrow R'X + R_2SnClX \qquad (3)$$

$$2R'Cl + R_2SnX_2 \longrightarrow 2R'X + R_2SnCl_2 \qquad (4)$$
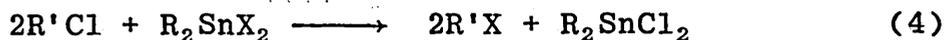
Klemchuk[70] studied the reactions of allylic and tertiary alkylchloride model compounds with organotin stabilisers in order to confirm the theory of Fry et al. It was concluded that the presence of allylic chlorine atoms in PVC may well be an influencing factor in the degradation process of the polymer and confirmed the formation of dialkylchlorotin derivatives as a product from reactions with the model compounds.

Ayrey et al[71] also confirmed that reactions (3) and (4) readily occur with model compounds at 180°C and in a later paper[49] studied the reactions of model compounds containing tertiary and allylic chlorine atoms with various organotin mercaptides, thioglycollates and carboxylates and confirmed Klemchuk's conclusions on the nature of the process leading to degradation of the polymer.

Many workers, however, have concluded that the organotin stabiliser reacts with the liberated hydrogen chloride to form dialkyltin dichlorides. Stapfer and Gannick[72] studied the degradation process of PVC containing antioxidant stabilisers. It was recognised that dibutyltinbis(isooctylthioglycollate) functioned as a

potent antioxidant which imparted the best long-term stability and it was concluded that, after dehydro-chlorination, the stabiliser formed dibutyltin dichloride prior to degradation of the polymer.

Poller[73] studied the interactions between PVC and isotopically labelled stabiliser, $Bu_2Sn(^{35}SBu)_2$, during degradation and concluded that the dominant reaction in the stabilisation process was the absorption of hydrogen chloride to form dibutyltin dichloride. In a later review, Poller[74] suggested that the stabiliser performed two roles:

(i) during an induction period, the stabiliser functioned in a preventative way by exchanging allylic chlorine atoms present in the polymer with the thioglycollate groups, and

(ii) during the main degradation process it served to remove the liberated hydrogen chloride, forming dibutyltin dichloride and thiol which then adds across the double bonds in the polymer.

Wirth and Andreas,[55] in an extensive review of the process of stabilisation, have also concluded that the main factor in both thermal and photodegradation is the presence of labile allylic chlorine atoms which act as initial sites for the dehydrochlorination process.

Ayrey et al[75] have suggested that chlorine atom
initiators are generated in the induction period
preceding decomposition. The organotin stabilisers
delay the decomposition of the PVC by exchanging X-groups
(in R_2SnX_2 where X = OCOR, SR) for allylic chlorine
atoms and generation of HX compounds which add to the
double bonds formed to reduce the formation of long
polyene sequences.

1.5 MIGRATION AND EXTRACTION OF ORGANOTIN STABILISERS FROM POLY(VINYLCHLORIDE)

Organotin-stabilised PVC has proven itself to be an
important material in the food packaging industry in
the form of blister packaging,[13] blow moulded
bottles[76,77] and calendered sheet.[78]

A number of alkyltin thioglycollates and maleates
(R_2SnX_2, where R = Me, Bu, Oct and X = $SCH_2CO_2C_8H_{17}$ or
$O_2CCH=CHCO_2C_8H_{17}$) have wide acceptance as stabilisers
for food contact packaging[34,79,80] due to their low
mammalian toxicity[81] and low aqueous leachability.[74,82]

Long-term migration studies of dioctyltinbis(isooctyl-
thioglycollate) [1] from PVC bottles into liquid foods
was often found to be comparable to background levels of
tin in the foods before extraction, thus indicating the
low level of migration occurring.[83,84] After six months,
the amount of [1] which had migrated from PVC bottles
into sunflower oil was found to be less than 2 ppm[85] and
long-term extraction studies carried out by Koch[86] showed

that only 0.01 ppm of [1] was extracted by beer from PVC bottles at 20°C.

Organotin stabilisers are readily extracted from PVC food containers by olive oil, orange or lemon soft drink concentrate and 50% aqueous ethanol.[87] Migration of [1] and dioctyltinbis(isooctylmaleate) [2] into a variety of liquid foods has been measured at 57°C over a period of eight weeks,[88] levels of organotin in these materials ranged from 0.01 to 0.24 ppm. No additional changes in the levels of migration were found when the study was extended at room temperature to a full year in duration.

Stabiliser [1] could be detected in heptane and other solvents used to extract rigid PVC but could not be detected in coconut oil, triacetin, or triglyceride mixtures.[89]

Radiolabelling of stabilisers has proven to be a useful approach for studying organotin migration. The radio-labelled stabilisers methyltin-tri-, [3], dimethyltin-di, [4], and trimethyltin- isooctylthioglycollate, [5], ^{14}C labelled in both the methyltin or thioglycollate moiety, have been extracted with HB307 (a complex synthetic triglyceride mixture).[90] The total amount of intact stabiliser migrating into fat-containing foods was not exceeding 1 ng of [3], 73 ng of [4] and 39 ng of [5] per gram of food.

Methods of Organotin Detection

Detection of tin in foods is usually accomplished by oxidative destruction of the food followed by addition of HBr and HCl to form a tin halide which is then distilled and determined quantitatively by colourimetry.[91] Radiolabelling has been successfully used for quantifying migration.[90] Flameless atomic absorption has been used in a recent study of organotins extracted from PVC.[92] Atomic absorption spectroscopy has been used to detect octyltins extracted by water from PVC pipe[93] but, in this work, quantitive analysis of tin was complicated by precipitation of insoluble tin compounds.

A recent review by Senich[79] has shown that there is a lack of consensus in the food contact organotin migration literature, due to the analytical methods used, on whether the intact stabiliser or their degradation products migrate. None of the analytical methods used gives actual structural information for the migrating tin-species.

The undegraded organotin compound was found to migrate from PVC into hexane and lipid-based extractants while the major component migrating into aqueous extracts was an organotin oxide in the form of the cyclic trimer $(R_2SnO)_3$, together with minor amounts of the undegraded compound and a dihydroxy form, $R_2Sn(OH)_2$, also thought to be present.[94]

Migration of dioctyltin esters and other organotins into aqueous and fatty foods has been studied.[79] No chemical change in the octyltins was evident while for other organotins, mainly decomposition products were found to have been extracted.

Experiments with stabiliser [1], radiolabelled at the ester-or octyl-group, migrating into edible oils showed that the stabiliser migrates either undegraded from rigid PVC or following hydrolysis, as two components which migrate at the same rate.[96] The same material similarly radiolabelled has been the object of another study[97] in which it was concluded that the stabiliser, its three degradation products, isooctylthioglycollate, dioctyltin dichloride and oxide and their degradation products, all migrate into foods. Further studies with this radiolabelled stabiliser[82] showed that it did not migrate intact but diooctyltin dichloride and a dimer of isooctylthioglycollate ... could be found in small amounts in aqueous or fat simulants.

These conflicting results from the available literature suggest that no definite conclusions can be drawn on the chemical nature of the migrating species of the stabiliser [1].

The degradation processes which occur in γ-irradiated
PVC are similar to those which occur in thermal and
photochemical degradation of the polymer. Dehydro-
chlorination,[98-103] unsaturation,[99] peroxide formation,[100]
and formation of free radicals[104] occur with the resulting
discolouration of the polymer.

An excited molecule of PVC can form free radicals by
cleavage of C–H, C–C, or C–Cl bonds:

$$\sim \left[\begin{array}{cc} \underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}} & \underset{Cl}{\overset{H}{\underset{|}{\overset{|}{C}}}} \end{array} \right] \sim \longrightarrow \sim CH_2 - \overset{\bullet}{C}H - CH_2 \sim + \ Cl^{\bullet} \qquad (5)$$
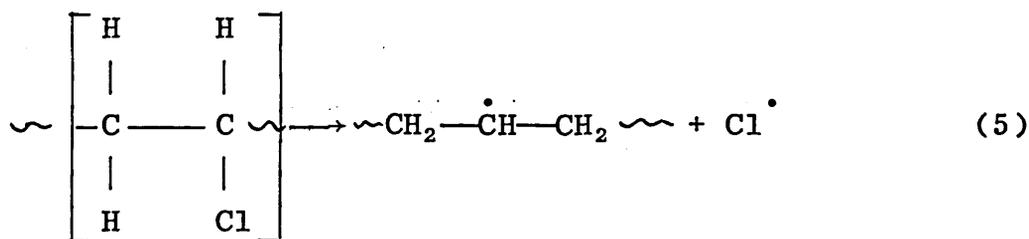
Table 1.2 indicates that the C–Cl bond (with the lowest
bond energy) is the most likely to break initially
(reaction (5)).

Table 1.2   Bond Energies for Poly(vinylchloride)

Bond Energies	(K cal/mole at 25 °C)
C− H	99
C− C	83
C− Cl	81

(Data obtained from reference 104)

From reaction (5) the formation of polyene sequences
can easily be explained:

$$Cl^\bullet + \sim CH-CH_2-CH-CH_2-CH-CH_2 \sim \longrightarrow \sim CH-CH_2-CH-CH-CH-CH_2 \sim + HCl \tag{6}$$

with Cl substituents on the indicated carbons.

$$\longrightarrow \sim CH-CH_2-CH-CH= CH-CH_2 \sim + Cl^\bullet \tag{7}$$

$$\longrightarrow \sim CH-CH= CH-CH= CH-CH_2 \sim + HCl \tag{8}$$

$$\longrightarrow \sim (CH=CH)_\eta \sim + \eta HCl \tag{9}$$
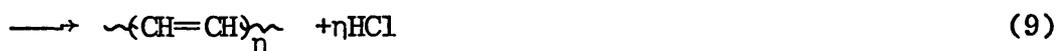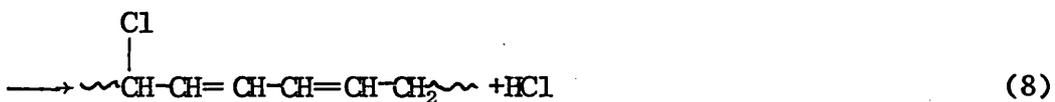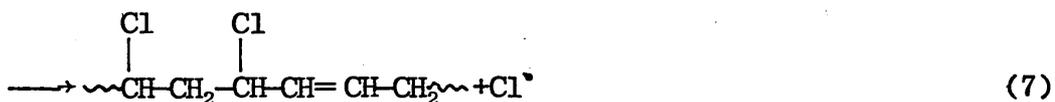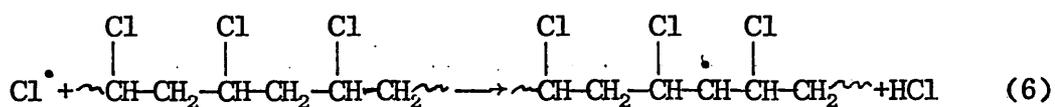
The radical formed in equation (6) is immediately
stabilised by formation of a double bond and another
chlorine radical is eliminated (equation (7)). As a
result an allylic chlorine atom is formed which is
labile, thus starting the 'unzipping' propagation.

Crosslinking of the polymer may occur by coupling of
adjacent free radicals produced in reaction (6). Both
crosslinking and chain scission have been reported during
γ-irradiation of PVC.[105-107]

It has been shown that the presence of oxygen has an
important influence on the γ-degradation of PVC. Polyene
chains with long sequences are formed as a result of
dehydrochlorination and produce intense colour in PVC
irradiated in vacuo.[108] Degradation under oxygen
causes a much lighter discolouration because polyene
formation is hindered by oxidative attacks on the conjugated

double bond system.[109] The radicals formed by the γ-irradiation react rapidly with oxygen to give peroxy-radicals which lead ultimately to the formation of carbonyl and hydroxyl groups.[98, 110-12] Some of the reactions which may occur have been studied by Ranby et al:[113]

$$\sim\!\sim CH_2\!-\!\overset{\bullet}{C}H\!-\!CH_2\!-\!CHCl\!\sim\!\sim +O_2 \longrightarrow \overset{\overset{\displaystyle O\!-\!O^{\bullet}}{|}}{CH_2\!-\!CH\!-\!CH_2\!-\!CHCl}\!\sim\!\sim \qquad (10)$$

$$\overset{\overset{\displaystyle O\!-\!O^{\bullet}}{|}}{\sim\!\sim CH_2\!-\!CH\!-\!CH_2\!-\!CHCl}\!\sim\!\sim \quad \underset{\longrightarrow}{\sim\!\sim CH_2\!-\!CHCl\sim\!\sim}$$

$$\overset{\overset{\displaystyle O\!-\!OH}{|}}{\sim\!\sim CH_2\!-\!CH\!-\!CH_2\!-\!CHCl}\!\sim\!\sim \; + \; \sim\!\sim\overset{\bullet}{C}H\!-\!CHCl\sim\!\sim$$

$$\downarrow$$

$$^{\bullet}OH \; + \; \sim\!\sim\overset{\overset{\displaystyle O^{\bullet}}{|}}{CH_2\!-\!CH\!-\!CH_2\!-\!CHCl}\sim\!\sim$$

$$\downarrow$$

$$\swarrow \qquad \searrow$$

$$\sim\!\sim CH_2C\!\!\diagdown\!\!\overset{\displaystyle O}{\underset{\displaystyle H}{}} \qquad\qquad \overset{\overset{\displaystyle OH}{|}}{\sim\!\sim CH_2\!-\!CH\!-\!CH_2\!-\!CHCl}\sim\!\sim$$

$$+ \qquad\qquad\qquad +$$

$$^{\bullet}CH_2CHCl\sim\!\sim \qquad\qquad \sim\!\sim\overset{\bullet}{C}H\!-\!CHCl\sim\!\sim$$
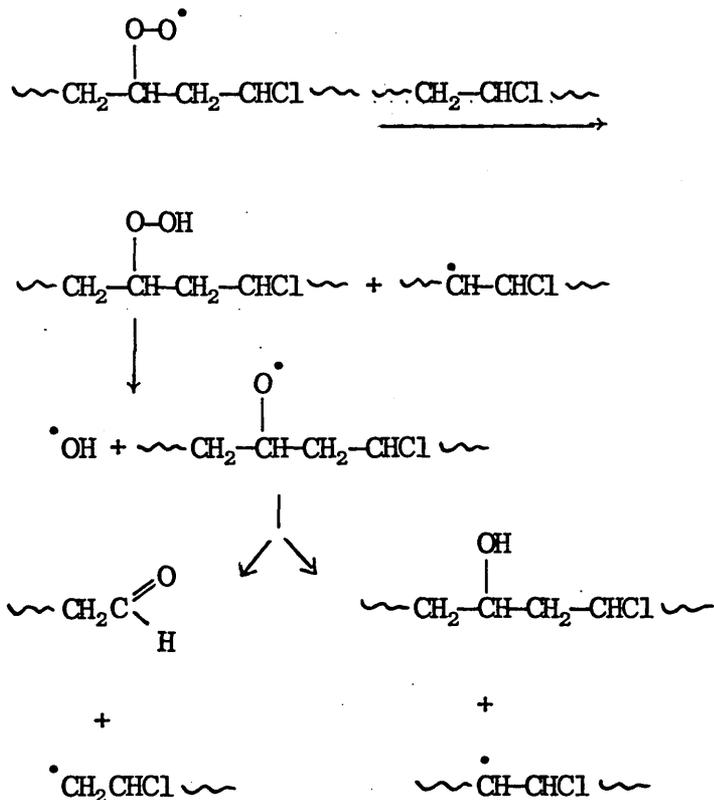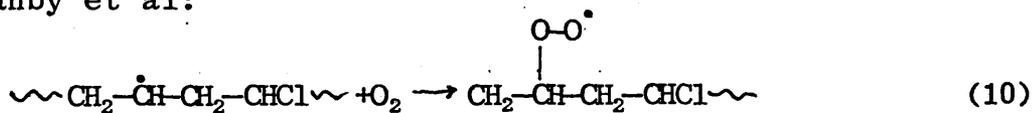
The extent of such reactions obviously depends on the thickness of the polymer and the ability of oxygen to diffuse into it during the irradiation process.

The use of organotin compounds as effective combined radiation and heat stabilisers has been recently reported.[114] It was shown that PVC formulations

containing octyltin stabilisers were successful in
preventing discolouration and loss of physical
properties on exposure to high dosage of γ-irradiation.
Rigid PVC containing five parts per hundred of organotin-
based additive prevented any perceptible discolouration
upon irradiation at a dose of 30 kGy and also prevented
the undesirable formation of hydrogen chloride.

There is little published work on the effect of
γ-irradiation on the stabiliser in the PVC matrix or the
possible stabilisation mechanism. However, the effect
of γ-irradiation on the migration of dioctyltinbis-
(isooctylthioglycollate) [1] from PVC into food simulants
has been studied[8,15] and some of the migration products
identified.

1.7 IDENTIFICATION OF ORGANOTIN-STABILISER DEGRADATION PRODUCTS IN GAMMA-IRRADIATED POLY(VINYLCHLORIDE)

In view of the proposed technique of food preservation
by γ-irradiation[1] and the use of organotin-stabilised
PVC for food packaging applications, the chemical
changes in the polymer additives have to be examined
and the likely migration products identified.

A recent study by Figge[8] used radiolabelled organotin
stabiliser [1], such that the migration into food
simulants, after irradiation, could be assessed. It was
recognised during this work that the components which
migrate, after irradiation, may have contained structurally
different material from the original additive. A similar

study by Haesen[115] has used various analytical techniques to determine the structures of the migrating organotin species from PVC both before and after irradiation. Conflicting results were obtained depending upon the analytical technique used. Insoluble and involatile tin-containing components remained unidentified. Atomic absorption measurements showed an increase in tin-containing migrants after γ-irradiation but could not be assigned to the identified degradation products.

The problem of determining the structural detail of tin-containing components as described above and those in Section 1.5 may be overcome by the use of ^{119}Sn Mössbauer spectroscopy. This technique can be used to observe directly the structural changes which organotin stabilisers undergo within a PVC matrix, thus avoiding the problems associated with the redistribution of chlorine and isooctylthioglycollate ligands between R_2SnX_2 centres (where X = Cl or isooctylthioglycollate), which are known to occur in solution.[117] In recent work, the technique of ^{119}Sn Mössbauer spectroscopy has been used to investigate changes which occur in the structures of organotin stabilisers as a result of thermal[117,118] or photochemical[119] degradation of PVC.

^{119}Sn Mössbauer studies of the thermal degradation of PVC containing the stabilisers R_2SnX_2 (where R = Bu or Oct and X = $SCH_2CO_2C_8H_{17}$ or $O_2C.CH=CHCO_2C_8H_{17}$) have shown that, in each case, the stabiliser is converted

into the dialkylmonochlorotin ester, R_2SnClX, and not to the dialkyltin dichloride, R_2SnCl_2, as suggested by other workers.[71-73]

This technique, if applied to γ-irradiated PVC containing organotin stabilisers, may indicate the actual structures of organotin degradation products and therefore the likely migration products into food products can be identified.

1.8   OBJECTIVES OF THE PRESENT STUDY

From the literature reviewed earlier, a number of clear objectives can be stated:

(i)   The determination of the chemical nature of tin-containing species produced by the γ-irradiation of organotin-stabilised PVC, in order to predict likely migration products which may present a toxicological hazard upon migration into food-stuffs.

(ii)   An assessment of the usefulness of commercially available organotin stabilisers as potential radiation stabilisers.

(iii)   The determination of the extent of degradation of the organotin stabilisers at irradiation doses likely to be used in commercial irradiation plants (up to 75 kGy).

(iv) The identification of the mechanism of
stabilisation/degradation of the organotin
stabilisers during irradiation.

(v) The determination of any chemical changes in the
polymer associated with the formation of
stabiliser degradation products.

1,9 REFERENCES

1. Report of Joint FAO/IAEA/WHO Expert Committee, WHO Technical Report Series, 1981, No 659.

2. E.S. Josephson, J. Food Safety, 1983, 5, 161.

3. E.S. Josephson, M.H. Thomas and W.K. Calhoun, J. Food Proc. Preserv., 1978, 2, 299.

4. J. Barna, Compilation of bioassay data on the wholesomeness of irradiated food items. Acta Alimentaria, 1979, 3, 205.

5. G. Hoeser and A. Schwarze, Plastics and Rubber : Materials and Applications, 1979, 93.

6. P.S. Elias, Chem. and Ind., 1979, 336.

7. G.O. Payne and C.C. Schmeige, Survey of Packaging Requirements for Radiation-Pasteurised Foods, USAEC Contract No. AT(11-1)-989, N.Y., USA : Cont. Can. Co. Inc., 1962.

8. K. Figge and W. Frewytag, Dtsch. Leberism. - R., 1977, 73, 7, 205.

9. Code of Federal Regulations, Title 21, Chapter I, Part 179.

10. J.J. Killoran, Radiation Res. Rev., 1972, 3, 369.

11. R. Leimgruber, paper presented at the 'International Conference on Advances in the Stabilisation and Controlled Degradation of Polymers', Zurich, 1983.

12. G.A. Senich, _Polymer_, 1982, _23_, 1385.

13. S. Karpel, _Tin and Its Uses_, 1984, 139, 10.

14. G. Ayrey, B. C. Head and R.C. Poller, _J. Polym. Sci., Macromol. Rev._, 1974, _8_, 1.

15. Z. Mayer, _J. Macromol. Sci., Rev. Macromol. Chem._, C10, 1974, 263.

16. D. Braun, In _"Degradation Stab. Polym., Proc."_, Plenary Main Lect. Int. Symp., 1974, (G. Geuskens, Ed), New York, John Wiley, 1975, p 23.

17. W.H. Starnes, _Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem._, 1977, _18_, p 493.

18. W.H. Starnes, _Adv. Chem. Ser._, 1978, _169_, 309.

19. E.D. Owen, _ACS Symp. Ser._, 1976, _25_, 208.

20. L.G. Close, R.D. Gilbert and R.E. Fornes, _Polym. Plast. Technnol. Eng._, 1977, _8_, 177.

21. H.O. Wirth and H. Andreas, _Pure Appl. Chem._, 1977, _49_, 627.

22. J.F. McKellar and N.S. Allen, Eds., _Photochemistry of Man-Made Polymers_, London, Applied Science, 1979, pp 95 -102.

23. W.H. Starnes, _Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Pap._, 1980, _42_, 716.

24. W.H. Starnes, In 'Developments in Polymer Degradation',
    Ed., N. Grassie, Applied Science Publishers, 1981,
    <u>3</u>, p 136.

25. R.J. Stimpel, <u>Popular Plastics</u>, 1973, <u>44</u>, 33.

26. D. Braun, In '<u>Degradation and Stabilisation of</u>
    <u>Polymers</u>', Ed., G. Gueskens, Applied Science,
    London, 1975.

27. B.B. Cooray and G. Scott, <u>Eur. Polym. J.</u>, 1980, <u>16</u>
    169.

28. D. Braun and M. Thallmaier, <u>Kunstoffe</u>, 1966, <u>56</u>, 80.

29. K.S. Minster, S.V. Kolesov and G.E. Zaikov,
    <u>J. Vinyl. Technol.</u>, 1980, <u>22</u>, 141.

30. B. Ranby and J.E. Rabek, <u>Photodegradation, Photo-</u>
    <u>oxidation and Photostabilisation of Polymers</u>,
    John Wiley, New York, 1975, p 192.

31. K.P.S. Kwei, <u>J. Polym. Sci.</u>, A1, 1969, <u>7</u>, 237.

32. K.P.S. Kwei, <u>J. Polym. Sci.</u>, A1, 1969, <u>7</u>, 1075.

33. G. Scott and M. Tahan, <u>Eur. Polym. J.</u>, 1975, <u>11</u>, 535.

34. B Ranby, J.E. Rabek, and G. Canback, <u>J. Macromol.</u>
    <u>Sci. Chem.</u>, A, 1978, <u>12</u>, 587.

35. J.C. Marchal, <u>J. Macromol. Sci. Chem.</u>, A, 1978, <u>12</u>,
    609.

36. C. Decker and M. Balandier, Polym. Photochem., 1981, 1, 221.

37. Z. Osawa and M. Aiba, Polym. Photochem., 1982, 2, 397.

38. G. Scott, J. Polym. Sci. Symp., 1976, 57, 357.

39. S.J. Blunden, P. Cusack and R. Hill, In 'The Industrial Uses of Tin Chemicals', Royal Society of Chemistry Publication, 1985, Chapter 7.

40. A. Michel and T .. Van. Hoang, Pure Appl. Chem., 1981, 53, 567.

41. G. Ayrey, F.P. Man and R.C. Poller, Eur. Polym. J., 1981, 17, 45.

42. B.B. Cooray and G. Scott, In 'Developments in Polymer Stabilisation', Ed. G. Scott, Applied Science, London, 1980, 2, p 53.

43. L.R. Brecker, Pure Appl. Chem., 1981, 53, 577.

44. W.H. Starnes, In 'Developments in Polymer Degradation', Ed., N. Grassie, Applied Science Publishers, 1981, 3, p 135.

45. Polymer Science and Technology, 1964-1972, 12, 725.

46. A.H. Frye, R.W. Horst and M.A. Paliobagis, J. Polym. Sci., A2, 1954, 1765.

47. J. Stepek and C. Jirkal, Chem. Listy., 1965, 59, 1201.

48. C.H. Fuschman, Stabilisation of Polymers and Stabilisation Processes, 1967, 20.

49. G. Ayrey, R.C. Poller and I.H. Siddiqui, J. Polym. Sci., A1, 1972, 10, 725.

50. S.Z. Abbas and R.C. Poller, Polym. Lett., 1974, 15, 543.

51. G. Genskens, Degradation and Stabilisation of Polymers, Applied Science, 1975, 1, 1.

52. G. Scott, Developments in Polymer Stabilisation, Applied Science, 1980, 2. 1.

53. J. Wypych, Die. Angew. Makromol. Chemie., 1975, 48, 1.

54. C.I. Balcombe, E. Elwood, C. Mullin and M.E. Peach, J. Inorg. Nucl. Chem., 1975, 37, 1353.

55. H.O. Wirth and H. Andreas, Pure and Appl. Chem., 1977, 49, 627.

56. D. Lanigan and E.L. Weinberg, Adv. Chem. Ser., 1976, 157, 134.

57. D. Lanigan, Proc. Int. Conf. PVC Processing, 1978, 4, 1.

58. G. Scott, M. Tahan, and J. Vyvoda, Eur. Polym. J.,
    1978, 14, 377.

59. W.H. Starnes, Adv. Chem. Ser., 1978, 169, 309.

60. N.D. Ghatge, Kautsch. Gummi Kunstst., 1979, 32, 254.

61. B.B. Cooray and G. Scott, Polym. Deg. and Stab.,
    1980, 2, 35.

62. B.B. Cooray and G. Scott, Eur. Polym. J., 1972, 16,
    169.

63. F. Alavi-Moyhadam, G. Ayrey and R.C. Poller, Polymer,
    1975, 16, 833.

64. V. Bellinger, J. Verdu and L.B. Caurette, Polym. Deg.
    and Stab., 1980, 3, 3.

65. M. Lequan, Y. Besace and R.C. Poller, Eur. Polym. J.,
    1980, 47, 141.

66. A.A. Caraculacu, E.C. Bezdadea and G. Istrate,
    J. Polym. Sci., A-1, 1970, 8, 1246.

67. K. Figge and W. Finders, Angew. Makromol. Chemie.,
    1975, 47, 141.

68. J.W. Burley, R.E. Hutton and V. Oakes, J. Organometal.
    Chem., 1978, 156, 369.

69. J.W. Burley, P. Hope, R.E. Hutton and C. Groenenboon,
    J. Organometal. Chem., 1979, 170, 21.

70. P. Klemchuk, Adv. Chem. Ser., 1968, 85, 1.

71. G. Ayrey, R.C. Poller and I.H. Siddiqui, Polym. Lett.,
    1970, 8, 1.

72. C.H. Stapfer and J.D. Gannick, J. Polym. Sci., A-1,
    1971, 9, 2625.

73. R.C. Poller, Adv. Chem. Ser., 1976, 157, 177.

74. R.C. Poller, J. Macromol. Sci.-Chem., A12, 1978, 3,
    373.

75. G. Ayrey, F.P. Man and R.C. Poller, J. Organometal.
    Chem., 1979, 173, 171.

76. R.R. Dean, Tin and Its Uses, 1975, 105, 11.

77. C.J. Evans, Tin and Its Uses, 1981, 130, 5.

78. C.J. Evans, Tin and Its Uses, 1975, 106, 9.

79. G.A. Senich, Polymer, 1982, 23, 1385.

80. Code of Federal Regulations, 1984, Title 21, Part 178,
    p. 18734.

81. S.J. Blunden, P. Cusack and R. Hill, In 'The Industrial
    Uses of Tin Chemicals', Royal Society of Chemistry
    Publication, 1985, Chapter 3.

82. K. Figge, W.F. Freytag and W.D. Beiber, Dtsch. Leberism-
    R., 1979, 75, 333.

83. H.G. Carr, Soc. Plast. Eng. J., 1969, 25, 72.

84. H.G. Carr, Soc. Plast. Eng. Tech. Pap., 1969, 15, 243.

85. H. Woggen, D. Jehle and W.J. Uhde, Nahrung, 1969, 13, 343.

86. J. Koch and K. Figge, Z. Lebensm.-Unters-Forsch., 1971, 147, 8.

87. C.A. Brighton, Plast. Polym., 1968, 36, 549.

88. W.P. Pinkasavage, 'Federal Regulatory Requirements for Octyltin Stabilised PVC in Food Packaging', Soc. Plast. Eng. Tech. Pap., Reg. Tech. Conf., Palisades Sect., Oct. 27-28, 1970, p 6.

89. K.G. Bergner and H. Berg, Dtsch. Leberism-R., 1972, 68, 282.

90. K. Figge, Verpack-Rundsch., 1975, 26, 59.

91. M. Farnsworth and J. Pekola, 'Tin', Eds., I.M. Kolthoff and P.J. Elving, In 'Treatise on Analytical Chemistry', Part 2A, Interscience, New York, 1961, 3, 327.

92. F. Taleb, M. Carrier and J. Vallon, J. Ann. Fals. Exp. Chim., 1979, 72, 441.

93. G.R. Dictz, J.D. Banzer and E.M. Miller, J. Vinyl. Technol., 1979, 1, 161.

94. W.C.H. Yen, 'Quantitative and Qualitative Study of the Migration of Organotin Stabiliser from PVC to Liquid Foods, Rutgers State Univ. New Jersey, New Brunswick, N.J., Dissertation, 1970.

95. H. Woggan, W.J. Uhde and H. Saeuberlich, Ernaehrungs-forschung, 1971, 16, 645.

96. H. Seidler, M. Haertig, H. Woggan and W.J. Uhde, Nahrung, 1971, 15, 187.

97. K. Figge and A. Zeman, Kunststoffe, 1973, 63, 543.

98. C. Decker, J. Appl. Polym. Sci., 1976, 20, 3321.

99. G. Lerke, I. Lerke and W. Szymanski, J. Appl. Polym. Sci., 1983, 28, 519.

100. I. Lerke and W. Szymanski, J. Appl. Polym. Sci., 1983, 28, 513.

101. I. Lerke and W. Szymanski, J. Appl. Polym. Sci., 1977, 21, 2067.

102. G. Lerke, I. Lerke and W. Szymanski, J. Appl. Polym. Sci., 1983, 28, 501.

103. A.H. El-Sayed, T. Seguchi and S. Machi, J. Appl. Polym. Sci., 1981, 26, 2947.

104. M. Foure and P.E. Rakita, Med. Device and Diagn. Ind., 1983, 5, 57.

105. A. Charlesby, Nature, 1953, 171, 167.

106. E.J. Lawton, A.M. Bueche and J.S. Balwit, Nature, 1953, 172, 76.

107. A. Chapiro, J. Chim. Phys., 1956, 53, 895.

108. G.J. Atchison, J. Appl. Polym. Sci., 1963, 7, 1471.

109. A.A. Miller, J. Phys. Chem., 1959, 63, 1775.

110. S. Ohnishi, S. Sugimoto and I. Nitta, J. Polym. Sci., A1, 1963, 625.

111. R. Salovoy and R.G. Beganer, J. Polym. Sci., A1, 1972, 10, 1533.

112. G. Zeppenfield and A. Bartl, J. Polym. Sci., 1969, 11, 4369.

113. B. Ranby, J.F. Rabek and G. Ganback, J. Macromol. Sci. Chem., A12, 1978, 4, 587.

114. M. Foure and P.E. Rakita, Med. Device and Diagn. Ind., 1983, 5, 33.

115. G. Haesen, R. Depans, H. Van Tilbeurgh, B. Le Goff and F. Lox, J. Ind. Irradiation Tech., 1983, 1, 259.

116. S.J. Blunden, L.A. Hobbs, P.J. Smith, A.G. Davies and S. Beng Teo, J. Organomet. Chem., 1985, 282, 9.

117. D.W. Allen, J.S. Brooks, R.W. Clarkson, M.T.J. Mellor and A.G. Williamson, Chem. and Ind., (London), 1979, p 663.

118. D.W. Allen, J.S. Brooks, R.W. Clarkson, M.T.J. Mellor and A.G. Williamson, J. Organomet. Chem., 1980, 199, 299.

119. J.S. Brooks, R.W. Clarkson, D.W. Allen, M.T.J. Mellor and A.G. Williamson, Polym. Deg. and Stab., 1982, 4, 359.

CHAPTER 2 : THE MÖSSBAUER EFFECT, HYPERFINE INTERACTIONS

AND EXPERIMENTAL DETAILS

2.1   THE MÖSSBAUER EFFECT

2.1.1   Nuclear Resonance Absorption

2.1.2   Line Width of the Emitted Gamma-Ray

2.1.3   Recoil Energy Loss and Doppler Broadening

2.1.4   Energy and Momentum Transfer to the Lattice

2.1.5   Recoilless Fraction and Debye-Waller Factor

2.1.6   A Mössbauer Spectrum

2.2   THE HYPERFINE INTERACTIONS

2.2.1   The Isomer Shift

2.2.2   The Quadrupole Splitting

2.2.3   Isomer Shifts and Quadrupole Splittings
        for Tin Compounds

2.2.4   The Magnetic Hyperfine Interaction

2.3   EXPERIMENTAL DETAILS

2.3.1   Characteristics of a Useful Mössbauer Isotope

2.3.2   The Mössbauer Source

2.3.3   The Absorber Requirements, Preparation and
        Method of Gamma-Irradiation

The phenomenon of the emission and absorption of a gamma-ray photon without loss of energy due to recoil of the nucleus and without thermal broadening is known as the Mössbauer effect. This was discovered by Rudolph Mössbauer in 1957[1] and has subsequently had an important influence in many branches of physics and chemistry. Its unique feature is in the production of monochromatic electromagnetic radiation with a very narrowly defined energy spectrum, so that it can be used to resolve minute energy differences. The direct application of the Mössbauer effect to chemistry arises from its ability to detect slight variations in the energy of interaction between the nucleus and the extra-nuclear electrons.

It was Mössbauer's discovery that securing the emitting nucleus in an inert matrix at low temperatures gave a finite probability that the recoil momentum of the γ-ray would be transferred to the crystal as a whole and not to the single emitting nucleus. This will occur when the recoil energy of the nucleus, E_R, is less than the energy required to excite the vibrational energy levels in the lattice. Under these conditions, the recoil energy and Doppler broadening associated with the transition are characterised by the mass and random velocity of the whole crystal and are therefore made negligible so that the emitted line has essentially the energy and width defined by the transition, i.e. the emission will be recoilless. This effect therefore makes it possible to

obtain the full intrinsic resolution associated with the emitted γ-rays.

2.1.1 NUCLEAR RESONANCE ABSORPTION

Consider the process of resonance absorption in the tin nucleus. The isotope ^{119}Sn is produced from the radioactive decay process of the metastable precursor ^{119m}Sn. A simplified energy level diagram is shown in Figure 2.1 and shows that, following the normal radioactive decay process, the metastable nucleus will decay to ^{119}Sn in an excited state, ^{119}Sn*. The excited nucleus rapidly decays to ground state ^{119}Sn resulting in the emission of a 23.8 keV γ-ray.

A second ^{119}Sn nucleus in the ground state in the path of the emitted photon, under certain ideal conditions, can absorb the energy of the photon to become an excited tin nucleus. The ground state nucleus is referred to as the absorber and the original excited nucleus as the source. The process of resonant fluorescence occurs when both the emission and absorption energy profiles completely overlap.

(M_I)

$-11/2$ ——————————— ^{119m}Sn 245d

γ 65.66 keV

$+3/2$ ——————— (E_e) ^{119}Sn*

$\underrightarrow{\gamma\text{-ray}}$

23.8 keV

$+1/2$ ——————— (E_g) ^{119}Sn

Source   Absorber

Absorption

E_O Energy E_O

Emission Profile   Absorption Profile

Absorption

Superpositioning of
the Emission and
Absorption profiles
gives Resonant
Absorption

Energy

Resonant Absorption
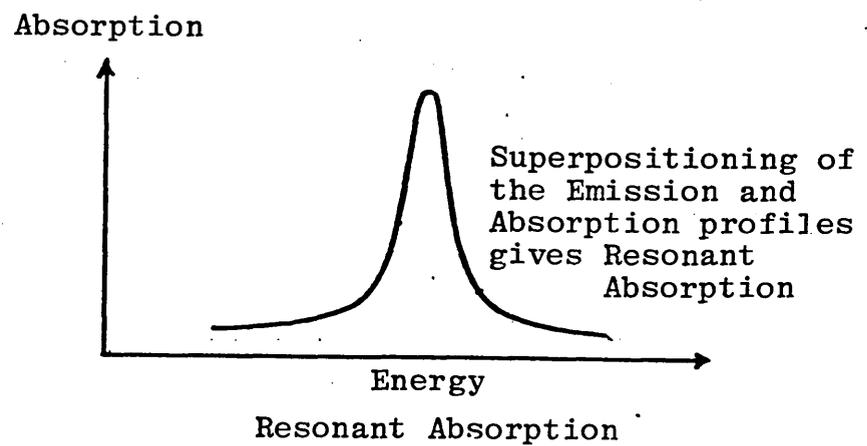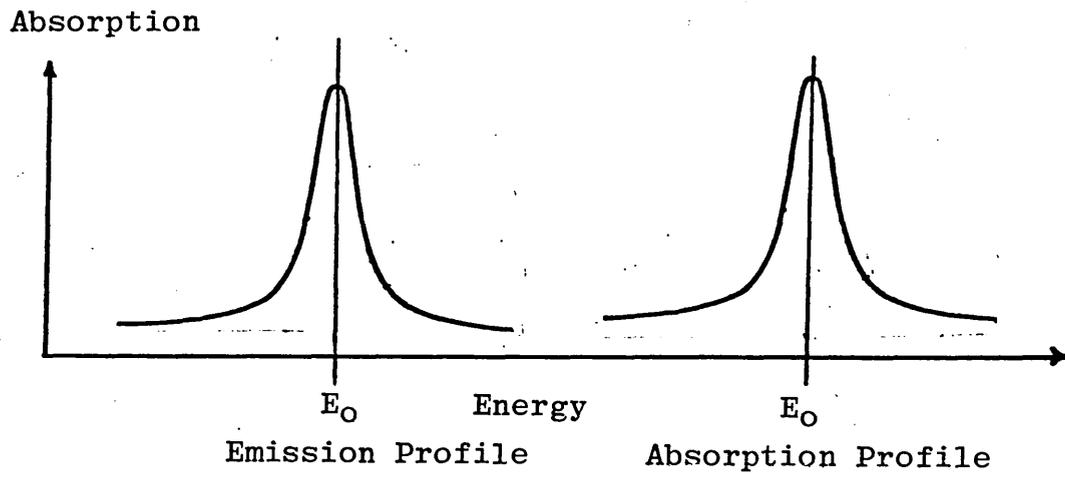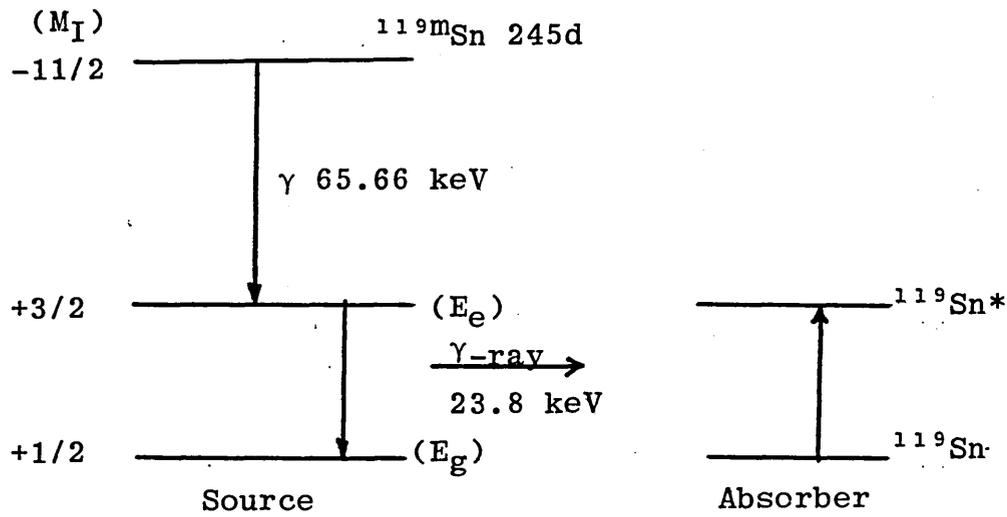
2.1.2 Line Width of the Emitted Gamma-Ray

The emitted γ-rays from the source have a Lorentzian energy distribution about a mean energy E_O and have a natural line width, Γ, as shown in Figure 2.2.
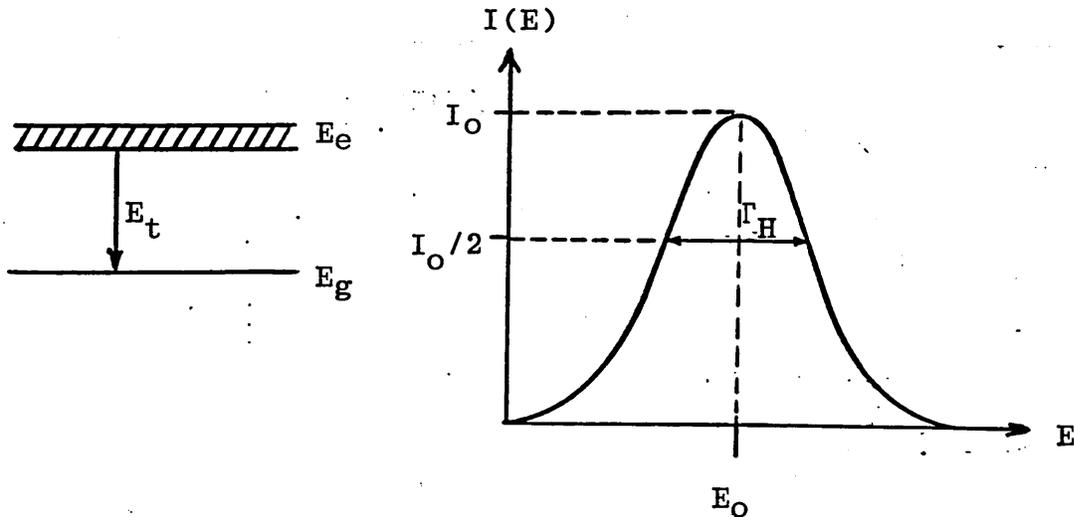
Figure 2.2 The Lorentzian distribution of emitted γ-rays

The energy distribution of the γ-rays is defined by the Breit-Wigner equation[2]:

$$I(E) = \frac{f_s \Gamma}{2\pi} \frac{1}{(E - E_O)^2 + (\Gamma/2)^2} \qquad (2.1)$$

where $I(E)$ = Intensity of the distribution at energy E.

f_s = Probability of Emission from the source.

Γ = Natural line width – determined from the Heisenberg Uncertainty Principle i.e.

$\Gamma = h/\tau$.

E_O = Transition energy.

τ = Mean lifetime of the excited state

$(= t_{\frac{1}{2}}/0.693)$

One of the most important influences on the γ-ray energy distribution is the mean lifetime of the excited state (τ). The ground state nuclear energy level has an infinite lifetime and therefore zero uncertainty in energy whereas the excited state has a mean lifetime of typically $10^{-6} - 10^{-10}$ s, so that there will be a spread of γ-ray energies of width Γ_H at half-height (Γ_H is defined as twice the natural line width ($= 2\Gamma$)).

The full width at half-height also determines the resolution of the technique. For example, for ^{119}Sn which has an excited state of mean lifetime 2.56×10^{-8}s then $\Gamma_H = 2.55 \times 10^{-8}$ eV.

If the transition energy is 23.8 keV then:

$$\frac{\Delta E}{E} = \frac{\Gamma_H}{E} = \frac{2.56 \times 10^{-8}}{23.8 \times 10^3} = 10^{-12}$$

i.e. a resolution of 1 part in 10^{12} is theoretically possible.

2.1.3 Recoil Energy Loss and Doppler Broadening

In the discussion of nuclear resonance absorption, it was assumed that as a result of the transition from the excited nuclear energy level to the ground state energy level, the emitted photon has an energy, E_γ, equal to the transition energy, E_t, ie $E_\gamma = E_e - E_g$.

In general, this is not so. If the photon is emitted from a nucleus of mass M moving with an initial velocity V_x in the chosen x-direction at the moment of emission,

then its total energy above the ground state nucleus at rest is $(E_e + \frac{1}{2}MV_X^2)$. After emission the γ-ray will have an energy E_γ and the nucleus a new velocity $(V_X + v)$ due to recoil (see Figure 2.3).

	Before Emission		After Emission
Velocity	$V \longrightarrow$		$V_X + v$ $\longrightarrow$
Energy	$E + \frac{1}{2}MV_X^2$	$=$	$E_\gamma + \frac{1}{2}M(V_X + v)^2$
Momentum	MV_X	$=$	$M(V_X + v) + E_\gamma/c$
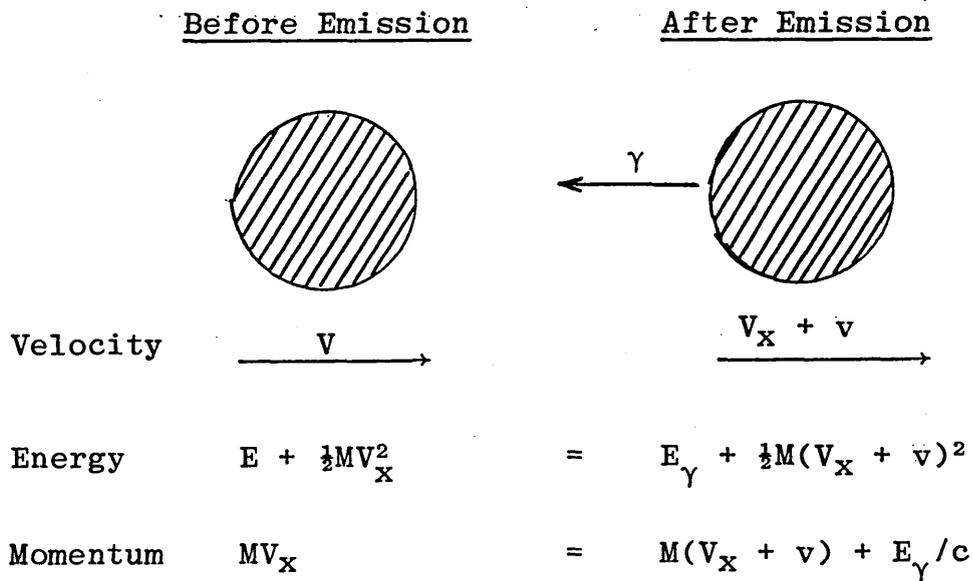
Figure 2.3 The energy and momentum conserved in the γ-emission process

By conservation of energy:

$$E_e + \frac{1}{2}MV_X^2 = E_g + E_\gamma + \frac{1}{2}M(V_X + v)^2 \qquad (2.2)$$

Since $E_t = E_e - E_g$ then $\qquad\qquad\qquad\qquad\qquad (2.3)$

$$\delta E = E_t - E_\gamma = \frac{1}{2}MV_X^2 + MvV_X \qquad (2.4)$$

$$\therefore \quad \delta E = E_R + E_D \qquad\qquad\qquad (2.5)$$

The γ-ray energy is thus seen to differ from the nuclear energy level separation by an amount which depends firstly on the recoil kinetic energy ($E_R = \frac{1}{2}MV^2$) which is independent of the velocity V_X, and secondly on the

term $E_D = MvV_x$ which is proportional to the atom velocity V_x and is a Doppler-effect energy. Consequently, emission of the γ-ray from the source results in a shift in energy of the emission energy profile of the order

$E_\gamma = E_t - E_R$. For resonance absorption to occur, a γ-ray energy of $E_\gamma = E_t + E_R$ is required, hence there is an energy difference of $2E_R$. The effect of E_R on the emission and absorption energy distributions is shown in Figure 2.4.
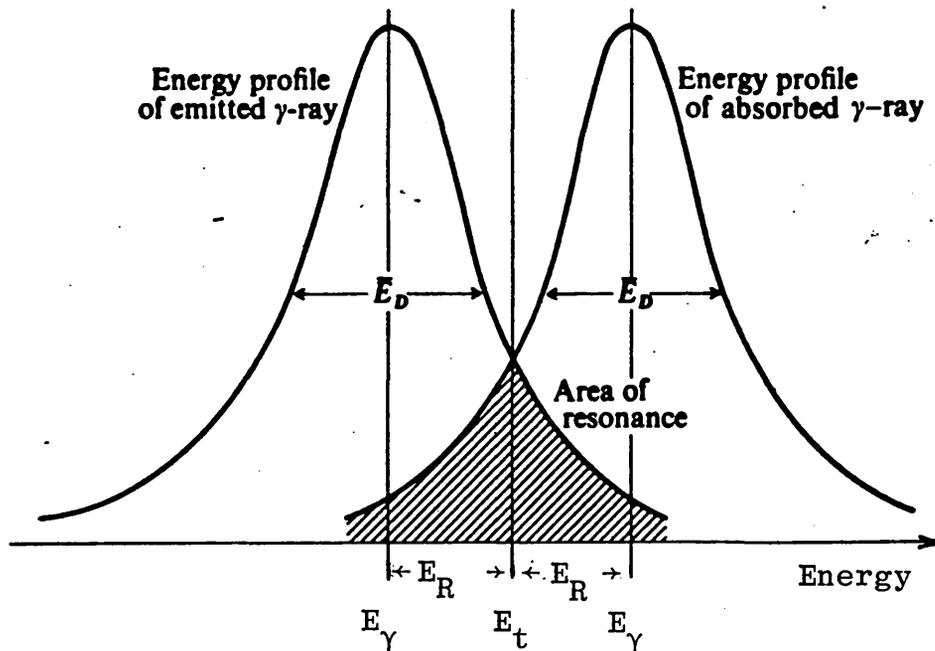
Figure 2.4 The effect of Thermal Doppler broadening and Recoil on the energy profiles of emitting and absorbing nuclei

In addition, the emission and absorption energy profiles experience Doppler broadening, E_D, arising from random thermal velocities of the source and absorber.

The kinetic energy of a nucleus in the x-direction from recoil is given by:

$$E_K = \tfrac{1}{2}MV_x^2 \approx \tfrac{1}{2}KT \qquad (2.6)$$

$$\text{and} \quad (V_x^2)^{\tfrac{1}{2}} = \sqrt{\frac{2E_K}{M}} \qquad (2.7)$$

Substituting for $(V_x^2)^{\tfrac{1}{2}}$ in (2.4) gives

$$E_D = 2\sqrt{E_R \cdot KT} \qquad (2.8)$$

Thus the γ-ray distribution is shifted by the magnitude of E_R and broadened by twice the mean of the recoil energy and the average thermal energy. The probability that resonance will occur depends on the magnitude of E_R. For transition energies of the order 10^4 eV, E_R is significant and overlap of the energy profiles is poor. In order to observe resonance absorption, it is necessary to eliminate the effects of recoil and Doppler broadening.

2.1.4 Energy and Momentum Transfer to the Lattice

In 1958 Mössbauer observed that the recoil energy loss could be significantly reduced by making the effective recoiling mass equal to the mass of the whole lattice rather than the mass of the nucleus, and by cooling the source and absorber to low temperatures, E_R and E_D become negligible and line widths approach the natural line width

of the nuclear transition. In the case of ^{119m}Sn Mössbauer spectroscopy the source is placed in an inert lattice (usually barium stannate) and the absorber is cooled to liquid nitrogen temperatures.

In the Einstein model of the lattice, the solid is considered as a quantum mechanical system in which its energy is quantised and transitions within the system occur through phonon interactions. The Einstein energy E_e is the minimum energy required to excite the lattice and corresponds to a single phonon transition. The vibrational energy of the lattice as a whole can only change by discrete amounts 0, $\pm h\omega$, $\pm 2h\omega$ etc, ($h\omega = E_e$ the Einstein energy), and depending on its magnitude, the recoil energy of a single nucleus can be taken up either by the whole crystal or it can be transferred to the lattice through phonon interactions thereby increasing the vibrational energy of the crystal. If the recoil energy is less than E_e then a zero phonon interaction occurs and no energy is transferred to the lattice and the recoil is taken up by the whole crystal. If the recoil energy is greater than E_e, then many phonon interactions may be involved and the energy is transferred to the vibrational energy of the lattice. Consequently the emitted γ-ray suffers energy recoil and is Doppler broadened. If a fraction 'f' of γ-photons are emitted without transfer of recoil energy to the vibrational states of the lattice (zero-phonon transitions), then a fraction (1 - f) will transfer one phonon $h\omega$. Thus f

will be greater the smaller the probability of exciting lattice vibrations, ie the smaller the γ-ray energy, the firmer the bonding of the atom in the lattice and the lower the temperature.

Lipkin[3] has shown that, if many emission processes are considered, the average energy transferred per event is exactly the free atom recoil energy, i.e.

$$E_R = (1 - f)\hbar\omega \qquad (2.9)$$

$$f = \frac{1 - E_R}{\hbar\omega} \qquad (2.10)$$

The above discussion represents a considerable simplification of the actual situation, i.e. a single lattice vibration frequency corresponds to an Einstein solid. A Debye model is more realistic, and includes frequencies ranging from zero to a maximum value ω_D.

2.1.5 Recoilless Fraction and Debye-Waller Factor

The probability W of zero-phonon γ-emission from a nucleus embedded in a solid which simultaneously changes its vibrational state can be calculated by dispersion theory[3,4], it is proportional to the square of the matrix element connecting the initial $|i\rangle$ and final $\langle f|$ states:

$$W = \text{constant} \times |\langle f| \mathcal{H} |i\rangle|^2 \qquad (2.11)$$

where $\mathcal{H}$ is the interaction Hamiltonian operator and depends upon the positional coordinates of the atom

(nucleus) and the momenta and spins of the particles within the nucleus. The forces acting within the nucleus are short range whereas those holding the lattice together are much longer range.[5] Hence the nuclear decay is independent of the vibrational state enabling the matrix element to be split into two parts of which the nuclear part will be constant depending only on the properties of the particular nucleus. The matrix element can now be reduced to the one term for the transition from the initial vibrational state L_i to the final state L_f. The form of the operator is such that:

$$W = \text{const} \times |\langle L_f | e^{i k \cdot x} | L_i \rangle|^2 \qquad (2.12)$$

where k is the wave vector for the emitted γ-photon and x is the co-ordinate vector of the centre of mass of the decaying nucleus. For zero-phonon emission, the lattice modes are unchanged and hence the probability for recoilless emission is:

$$f = \text{constant} \times |\langle L_i | e^{i k \cdot x} | L_i \rangle|^2 \qquad (2.13)$$

and since L_i is normalised $f = e^{-k^2 \cdot x^2}$. Since x is a random vibration vector, x^2 can be replaced by $\langle x^2 \rangle$, the component of the mean square vibrational amplitude of the emitting atom in the direction of the γ-ray. Since $k^2 = 4\pi^2/\lambda^2 = E^2_\gamma/(hc)$, where λ is the wavelength of the γ-ray we obtain:-

$$f = \exp\frac{(-4\pi^2 \langle x^2 \rangle)}{\lambda^2} = \exp\frac{(-E^2_\gamma \cdot \langle x^2 \rangle)}{(\hbar c)^2} \qquad (2.14)$$

Equation (2.14) indicates that the probability of zero-phonon emission decreases exponentially with the square of the γ-ray energy. This places an upper limit on the usable E_γ. Equation (2.14) also shows that f increases exponentially with the decrease in $\langle x^2 \rangle$ which in turn depends on the firmness of binding and on the temperature. A study of the temperature dependence of f affords a valuable means of studying the lattice dynamics of crystals and hence of obtaining additional structural information.

To proceed further, it is necessary to assume some model for the vibrational modes of the crystal. The simplest is due to Einstein (1907) and assumes the solid to be composed of a large number of independent linear harmonic oscillators each vibrating at frequency ω_E. The appropriate integral of equation (2.13) gives:

$$f = \exp\left[\frac{-E_R}{\hbar\omega_E}\right] = \exp\left[\frac{-E_R}{k\Theta_E}\right] \qquad (2.15)$$

where Θ_E is a characteristic temperature of the lattice given by $k\Theta_E = \hbar\omega_E$.

If $E_R \ll k\Theta_E$ then $f \cong 1 - E_R/k\Theta_E$.

The Debye model (1912) abandons the idea of a single vibrational frequency and embodies a continuum of oscillator frequencies ranging from zero up to a maximum ω_D, and following the distribution formula $N(\omega) = \text{constant} \times \omega^2$. A characteristic temperature called the Debye

temperature Θ_D is defined as $\hbar\omega_D = k\Theta_D$ and the average frequency is $\overline{\hbar\omega} = \frac{3}{4}\hbar\omega_D$. Values of Θ_D are often assigned to chemical compounds but since the Debye model is grossly inadequate, even for many pure metals, the values for compounds are merely an indication of the comparative lattice properties.

The Debye model leads to[6]

$$k^2 \cdot x^2 = \frac{\hbar}{2M} \int_0^{\omega_D} \frac{N(\omega)}{\omega} \left[\coth \frac{\hbar\omega}{2kT} \right] d\omega \qquad (2.16)$$

which can be written in the more familiar form:

$$f = \exp\left[-\frac{6E_R}{k\Theta_D} \left\{ \frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} \frac{x\,dx}{e^x - 1} \right\} \right] \qquad (2.17)$$

This is often written as $f = e^{-2W}$. The factor W is normally called the Debye-Waller factor. An exact solution to (2.17) is not possible. However, several approximate solutions are of interest:

At low temperatures where $T \ll \Theta_D$, equation (2.17) can be reduced to the approximation:

$$f = \exp\left[\frac{-E_R}{k\Theta_D} \left\{ \frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2} \right\} \right] \qquad T \ll \Theta_D \qquad (2.18)$$

and at absolute zero $f = \exp\left[\frac{-3}{2} \frac{E_R}{k\Theta_D} \right]$ \qquad (2.19)

In the high temperature limit

$$f = \exp \left[\frac{-6E_R T}{k\Theta_D^2} \right] \qquad T \geqslant \tfrac{1}{2}\Theta_D \qquad\qquad (2.20)$$

We note that in the high temperature limit a plot of
lnf against T should be a straight line, the gradient
of which is determine by Θ_D^2.

2.1.6 A Mössbauer Spectrum

If γ-rays from the source are passed through an absorber
of identical material, the transmission of the γ-rays
in the direction of the beam will be less than expected
due to resonant absorption and subsequent re-emission
over a 4π solid angle. The effective E_γ value can be
altered by moving the source and absorber relative to
each other with a velocity V by means of an externally
applied Doppler velocity such that $E_\gamma = E_t + \frac{E_t + V}{c}$.
This enables the source energy profile to be scanned
across the absorption energy profile. The recoil—free
γ-ray energy of a typical Mössbauer transition is so
precisely defined that its line width is determined by
the Heisenberg Uncertainty Principle. It is therefore
possible to imagine a particular relative velocity
between source and absorber at which the γ-ray energy
from the source will exactly match the nuclear energy
level gap in the absorber and resonant absorption will
be at a maximum. For a source and absorber which are
chemically identical, the relative velocity required to
achieve resonance will be zero. Figure 2.5 shows a plot

(a)   Source Profile

Γ

E_t → Energy
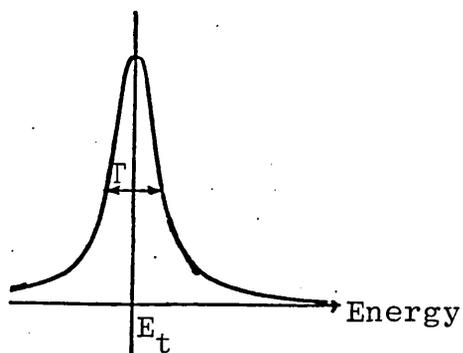
(b)   Absorption Profile

Γ

E_t → Energy
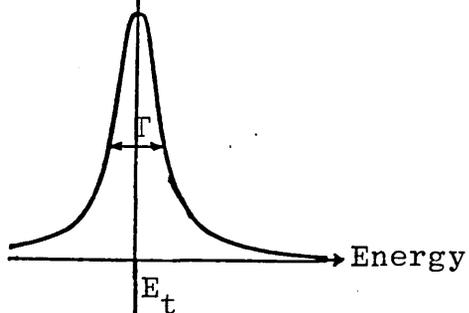
(c)   Source Profile moving
      at velocity v

Γ $E_t(1 + v/c)$

→ Energy

(d)   Mössbauer
      Spectrum

2Γ

−v   0   +v
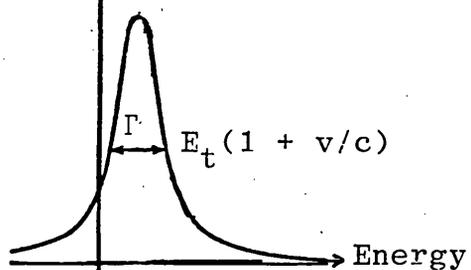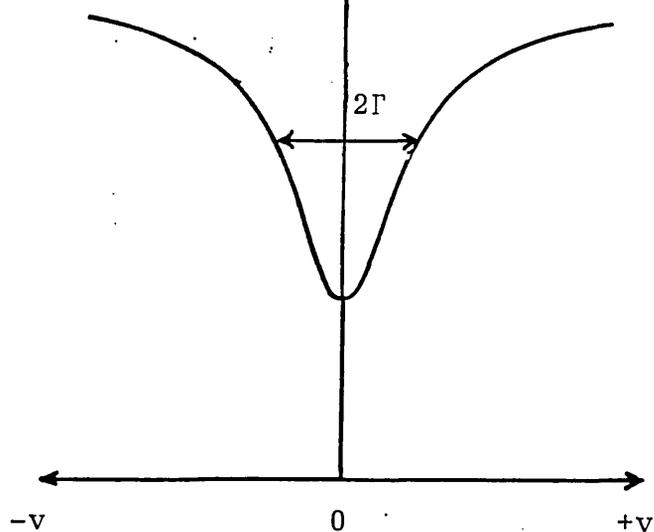
of absorption of a series of Doppler velocities between an identical source and absorber. The absorption line is Lorentzian in shape with a width at half-height corresponding to 2Γ. If the transition energy in the absorber is different to that in the source, then a greater or smaller Doppler velocity would have to be applied to achieve resonant absorption. Since these changes in nuclear energy levels in the absorber are directly related to the chemical environment of the absorbing nucleus, this facilitates a powerful method of measuring changes in the chemical environment in terms of Doppler velocity.

2.2 THE HYPERFINE INTERACTIONS

Application of the Mössbauer effect exploits its precise energy resolution. The natural line width of the Mössbauer radiation expressed as a fraction of the transition energy (Γ/E_O) may be as low as 5×10^{-16}. The line widths are comparable with or less than the interaction energies between the nuclei and their electronic environment. These interactions between the nucleus and its electronic environment are called Hyperfine Interactions.

It is normal to study the hyperfine interactions in absorbers containing the stable Mössbauer isotope using a single line source. The source matrix is chosen to have a line width as near to Γ as possible, and to have a large f-factor. The radioactive source is mounted on a

velocity transducer and the absorber fixed inside a
suitable cryostat (for ^{119}Sn). If the nuclear levels
in the absorber are split by the hyperfine interactions
then there will be a number of different energies at
which absorption can take place. The count rate of the
detector will drop whenever the Doppler velocity applied
to the source brings the emitted γ-ray into coincidence
with an absorption energy.

These hyperfine interactions give rise to the Isomer
Shift (δ), Quadrupole Splitting (ΔE_Q) and the Magnetic
Zeeman Splitting. All three interactions can be expressed
as the product of a nuclear term, which is constant for
a given Mössbauer γ-ray transition, and an electronic
term (as shown in Table 2.1), which is related to the
electronic structure of the resonant absorber being
studied.

2.2.1 The Isomer Shift

For many purposes it is adequate to consider the nucleus
as a point charge which influences the electrons via
the coulombic potential. However, the nucleus has a
finite volume, and this must be taken into account when
considering nucleus-electron interactions because an
s-electron wavefunction implies a non-zero electron
charge density within the nuclear volume. During the
course of a nuclear γ-transition, it is usual for the
effective nuclear size to alter, thereby changing the
nucleus-electron interaction energy. This change is only

Table 2.1 Schematic Representation of Hyperfine Interactions :

Magnetic Hyperfine Interaction + Electric Quadrupole Interaction + Isomeric Shift

Interaction	Magnetic Hyperfine Interaction	Electric Quadrupole Interaction	Isomeric Shift
	↓	↓	↓
Solid State Factor	Magnetic Field	Electronic Field gradient	Densities of Electrons at nuclear site
	↓	↓	↓
Nuclear Factor	Nuclear Magnetic Moment	Nuclear Quadrupole Moment	Mean square Nuclear Charge Radius

$$\Delta E = \mu H \quad + \quad Q \nabla E \quad + \quad \text{const} \langle R^2 \rangle \, \rho(O)$$

a minute fraction of the total coulombic interaction but
is dependent upon the chemical environment. Although
it is not possible to measure this energy change directly,
it is possible to compare values by means of a suitable
reference, i.e. the γ-ray source used in recording the
Mössbauer spectrum. The observed change in chemical
isomer shifts for a given nuclide is frequently within
an order of magnitude of the Heisenberg natural line
width of the transition. The Mössbauer resonance line
recorded by velocity scanning may thus be measurably
displaced from zero velocity if the chemical environment
of the nuclide in the source and absorber differ.

The isomer shift can be computed classically by
considering the effect of the overlap of s-electron
density with the nuclear charge density.

Only s-electrons have a finite probability of overlapping
with the nuclear charge density, and thus of interacting
with it; however, the s-electron density at the nucleus
is often sensitive to change in the p- or d-electron
density.

The nucleus is assumed to be a uniformly charged sphere
of radius R, and the s-electron density at the nucleus,
$[\psi(0)_s]^2$, is assumed to be constant over the nuclear
dimensions. By computing the difference between the
electrostatic interaction of a point nucleus and the
interaction of a nucleus having a radius R, the inter-
action energies can be estimated[6-8]. The difference in

energy is given by:

$$\delta E = K[\Psi(O)_s]^2 R^2 \qquad (2.21)$$

where K is a nuclear constant. Since R is generally different for ground and excited nuclear states, δE will be different for both (Figure 2.6), and:

$$\delta E_e - \delta E_g = K[\Psi(O)_s]^2 (R_e^2 - R_g^2) \qquad (2.22)$$

where subscripts e and g refer to the excited and ground nuclear states respectively. The R values are nuclear constants, but the $[\Psi(O)_s]^2$ values will vary from compound to compound. The above energy difference becomes measurable in the Mössbauer experiment by comparing the nuclear transition energy in the source ($^S E_\gamma$) with that in the absorber ($^a E_\gamma$). The isomer shift is given by the difference in transition energies for source and absorber:

$$\text{I.s.} = K(R_e^2 - R_g^2)\{[\Psi(O)_s]_a - [\Psi(O)_s]_s^2\} \qquad (2.23)$$

Usually the source is a standard material (e.g. $BaSnO_3$ for ^{119m}Sn Mössbauer spectra). Since the change in radius $R_e - R_g$ is very small, the isomer shift can then be written in its usual form:

$$\text{I.s.} = 2KR^2 \frac{\delta R}{R} \{[\Psi(O)_s]_a^2 - c\} \qquad (2.24)$$

where: $\delta R = R_e - R_g$ and c is a constant characteristic of the source used. Thus the isomer shift depends on a nuclear factor δR and an extra-nuclear factor $[\Psi(O)_s]_a^2$.

Figure 2.6 Nuclear energy levels and the isomer shift
(a) source and absorber nuclear energy
levels, (b) resultant Mössbauer spectrum

$^{a}E_{\gamma} > {}^{s}E_{\gamma}$
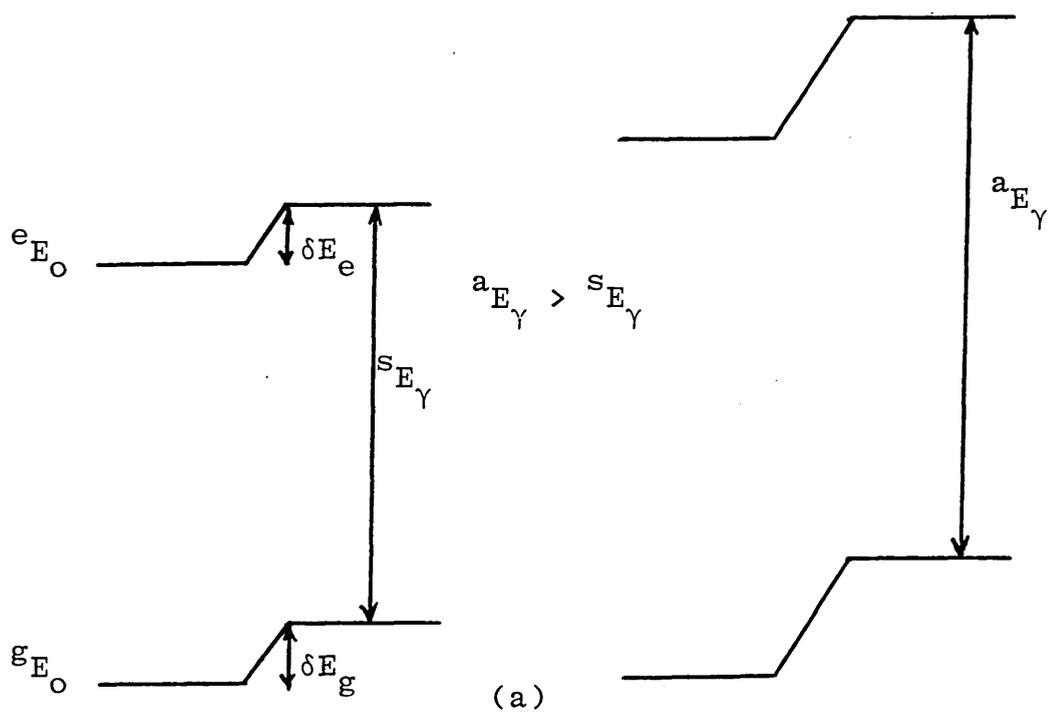
Single line source   Single line absorber

(a)

Absorption

Isomer shift = $^{a}E_{\gamma} - {}^{s}E_{\gamma}$

Velocity (mms^{-1})

−v   0   +v
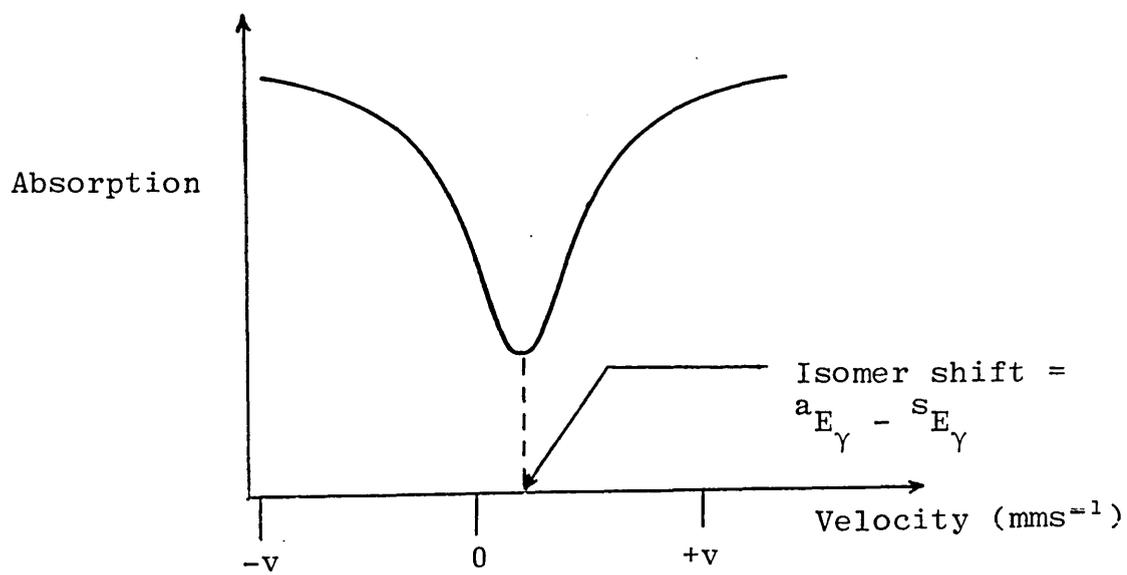
(b)

For a given nucleus, δR is a constant, so that the isomer shift is directly proportional to the s-electron density at the nucleus of the absorber. When δR is positive (as for ^{119}Sn), an increase in s-electron density at the absorber nucleus results in a more positive isomer shift; where δR is negative (as for ^{57}Fe), an increase in s-electron density at the absorber nucleus results in a more negative isomer shift.[6]

Although changes in isomer shift are due to variations in s-electron density, differences in isomer shifts are observed on addition or removal of p- or d-electrons which do not themselves interact directly with the nuclear charge density. Shielding by other electrons effectively increases the s-radial functions and decreases the s-density at the nucleus i.e. a $3d^6 4s^1$ outer configuration will have a higher s-density than $3d^7 4s^1$ because of the penetration of the 3d-orbitals into the 3s.

2.2.2 The Quadrupole Splitting

The quadrupole splitting arises from the interaction of the nuclear quadrupole moment with the local electric field gradient. In defining the interaction that gave rise to the isomer shift, the nucleus was considered to be spherical with a uniform charge density, i.e. the spin angular momentum (I) $=$ 0 or $\frac{1}{2}$, resulting in a zero quadrupole moment. For nuclei with a spin angular momentum greater than $\frac{1}{2}$ the charge density is no longer uniform and the nucleus assumes either a prolate or an

oblate shape, resulting in a discrete quadrupole
moment. The quadrupole interaction results in a splitting
of the nuclear energy levels. For ^{57}Fe and ^{119}Sn,
$I_e = \frac{3}{2}$ and $I_g = \frac{1}{2}$, and the $I = \frac{3}{2}$ level splits into two
($m_I = \pm \frac{3}{2}, \pm \frac{1}{2}$) while the $I = \frac{1}{2}$ levels remain degenerate.
Both the possible transitions are allowed with equal
probability and a characteristic two line spectrum is
obtained. In general, there will be a combined isomer
shift and quadrupole interaction (see Figure 2.7).
The separation of the peaks is the quadrupole splitting
and the centre of the two peaks relative to zero velocity
is the isomer shift. For half integral nuclear spins,
the quadrupole interaction results in $(I + \frac{1}{2})$ levels
for spin I.

The quadrupole interaction results in an energy change
given by:

$$E_Q = \frac{e^2 qQ}{4I(2I - 1)} [3m_I^2 - I(I + 1)](1 + \eta^2/3)^{\frac{1}{2}} \quad (2.25)$$

where Q   = nuclear quadrupole moment

      η   = asymmetry parameter

     m_I = magnetic quantum number

     eq   = maximum value of the field gradient

     e   = electronic charge

In each case where the degeneracy is removed, the magnitude
of the splitting is determined by the interaction of
the quadrupole moment with the Z component of the
electric field gradient (E.F.G.) which is related to the

Figure 2.7 Nuclear Energy levels and the quadrupole splitting - (a) Absorber energy levels : excited level $(I = \frac{3}{2})$ split into two by quadrupole interaction, (b) resultant Mössbauer spectrum

(a)

m_I

$\pm 3/2$

ΔE_Q

I

$3/2$

$\pm \frac{1}{2}$

$\pm \frac{1}{2}$

$1/2$ Isomer Shift   Quadrupole Splitting

Absorption

Quadrupole
Splitting

Isomer shift

(b)

Velocity
(mms^{-1})

$-v$ 0 $+v$
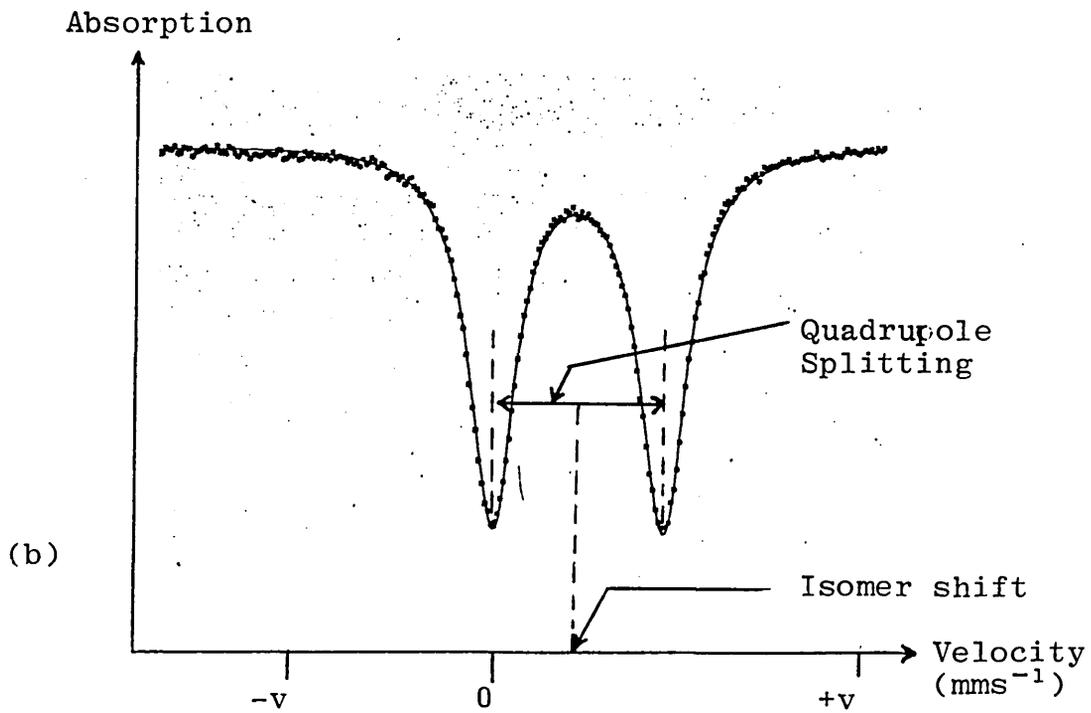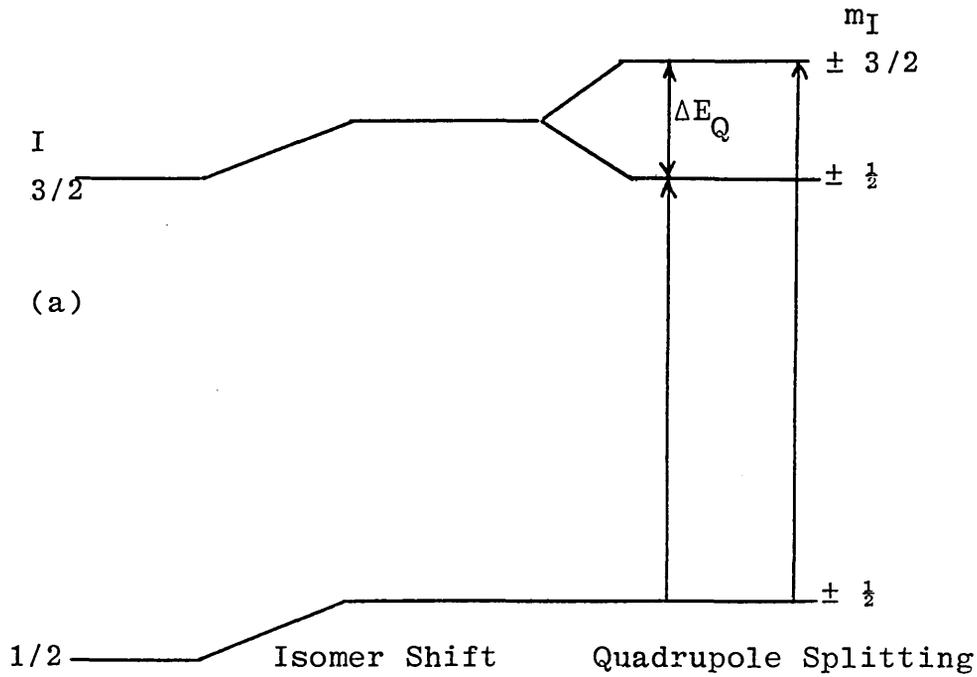
symmetry properties of the crystal. The E.F.G. is
found by applying the gradient operator to the three
components of the electric field which is itself a
vector. The result is a 3 x 3 tensor which can be
reduced to 3 components:

$$\frac{\partial^2 V}{\partial x^2}, \frac{\partial^2 V}{\partial y^2}, \frac{\partial^2 V}{\partial z^2} \quad \text{written } V_{xx}, V_{yy}, V_{zz}$$

These are not independent and are related by the Laplace
equation in a region where the charge density vanishes:
$V_{xx} + V_{yy} + V_{zz} = 0$. By convention the Z-coordinate
of the E.F.G. is chosen to coincide with the highest
symmetry axis of the molecule or crystal and η is defined
as:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \tag{2.26}$$

Thus V_{zz} and η are the only two independent components
in equation (2.25). The components are chosen so that
$V_{zz} \geqslant V_{yy} \geqslant V_{xx}$, thereby making $0 \leqslant \eta \leqslant 1$. For an axially
symmetric field gradient $V_{xx} = V_{yy}$ and so $\eta = 0$, and for
cubic or spherical symmetry each $V_{ii} = 0$ and the quad-
rupole interaction is zero.

The E.F.G. has two sources: firstly each electron in the
atom makes a contribution to a component of the E.F.G.
tensor, and if the orbital population is not spherical,
the total value of V_{zz} will be non-zero. This is termed
the valence contribution (q_{val}); and secondly there is
also a contribution from distant charges (ionic charges)

associated with ligands and is referred to as the lattice contribution (q_{lat}). These two contributions are not independent due to shielding/antishielding effects.

2.2.3 Isomer Shifts and Quadrupole Splittings for Tin Compounds

(a) Isomer Shifts

As described in Section 2.2.1, the isomer shift is largely determined by the s-electron density which penetrates the nucleus. The contributions by p-electrons are relatively small and are usually ignored.[9] It is also generally assumed that the contribution by the inner shells of the Sn atom is constant and that changes in isomer shift reflect changes in the population of the valence shell 5s-orbital. Changes in the population of the valence p- and d-orbitals will affect the electron density at the nucleus by shielding, but this effect is relatively small. The isomer shift should therefore vary with the polarity of the tin-ligand bonds. Some dependence on the number and arrangement of the bonds is also found and these factors are discussed in turn.

1. Nature of the Tin-Ligand Bond

In a series of compounds with similar structures, the isomer shift reflects the nature of the tin-ligand bonds. As the electronegativity of the ligands increases, the bonds become more ionic and the tin atom more positive. The loss of valence shell electron density, particularly from the 5s-orbital, would be expected to lead to a decrease in the isomer shift. This trend is observed in Table 2.2 for both tetrahedral and six-coordinate tin.

Table 2.2 Isomer Shift Data for Tin(IV), mms^{-1}

Tetrahedral		Octahedral	
SnI_4	1.45	SnI_6^{2-}	1.24
$SnBr_4$	1.10	$SnBr_6^{2-}$	0.84
$SnCl_4$	0.80	$SnCl_6^{2-}$	0.51
Me_4Sn	1.31	SnF_6^{2-}	-0.36
Ph_4Sn	1.22	SnO_2	0.00

(Data presented by R.V. Parish, in Progress in Inorganic Chemistry, S.J. Lippard, Ed., Wiley-Interscience, 1971, 15, p 132).

A correlation of the isomer shift with ligand electro-negativity and number of halide ions bound to tin[10] shows a linear relationship between the isomer shift for $SnX_4Y_2^{2-}$ (X, Y = Cl, Br, I) and the sum of the Pauling electro-negativities of the halogens bound to tin. The slope of this line was found to be 1.5 times that for the tetrahalides SnX_4.

Inspection of Table 2.3 shows that, within any series of organotin halides, the isomer shifts are reasonably constant (except for the fluorides which give constantly lower values). The reduced sensitivity of the isomer shift has been attributed to the much greater covalency of the R-Sn compared with the Sn-X bonds.[11]

In the series of compounds R_3SnY, in which the tin atom

Table 2.3 Isomer Shift Data for Organotin Halides, mms^{-1}

Organotin Compound	Halide	Methyl	Ethyl	n-Propyl	n-Butyl	Phenyl
R_3SnX	Fluoride	1.24	1.41	1.44	1.42	1.23
	Chloride	1.47	1.49	1.62	1.53	1.34
	Bromide	1.41	1.52	1.50	1.61	1.33
	Iodide	1.48	1.56	1.52	1.47	1.26
R_2SnX_2	Fluoride	1.31	1.42	1.45	1.42	1.28
	Chloride	1.55	1.64	1.70	1.62	1.38
	Bromide	1.59	1.74	–	1.64	1.43
	Iodide	–	1.72	–	1.80	1.51

(Data presented by R.V. Parish, in Progress In Inorganic Chemistry, S.J. Lippard, Ed., Wiley-Interscience, 1971, 15, p 140)

is 4-coordinate, the isomer shift is insensitive to the nature of Y, although quadrupole splitting data indicate wide variations in the polarity of Sn-Y bonds as shown in Table 2.4.

Two complementary effects could explain the constancy of the isomer shifts.[12] When an organic group is replaced by a more electronegative ligand, some rehybridisation might take place, which would increase the s-character of the Sn-C bonds, which are the most covalent bonds. The Sn-X bond will increase in p-character, so that more p-electron density than s-density is lost. Decrease of p-electron density increases the isomer shift by decreasing the shielding of the s-electrons. At the same time, the removal of electron density renders the tin atom more positive and increases the effective nuclear charge felt by the remaining electrons. The resulting contraction of the orbitals and increased covalency of the bonds, particularly the tin-carbon bonds, will compensate for the above decrease in shielding of the s-electrons.

In the series R_nSnX_{4-n}, the isomer shift would be expected to increase regularly with increasing n. This expectation is only partially realised for the organotin halides, since the isomer shift reaches a maximum at n = 2.

Table 2.4 Mössbauer Data for R_3SnY, mms^{-1}

Methyl Compounds	δ	Δ	Phenyl Compounds	δ	Δ
Me_4Sn	1.31	0	Ph_4Sn	1.22	0
$Me_3SnC_6Cl_5$	1.32	1.09	$Ph_3SnC_6Cl_5$	1.27	0.84
$Me_3SnC{\equiv}CPh$	1.23	1.17	$Ph_3SnC_6F_5$	1.31	0.90
$Me_3SnCCl=CCl_2$	1.31	1.24	Ph_3SnI	1.26	2.09
$Me_3SnC_6F_5$	1.27	1.31	Ph_3SnBr	1.33	2.48
Me_3SnCF_3	1.31	1.38	Ph_3SnCl	1.34	2.48

(Data presented by R.V. Parish, in Progress In Inorganic Chemistry, S.J. Lippard, Ed., Wiley-Interscience, 1971, 15, p 141)

2. Coordination Number

In general, an increase in the coordination number of the tin atom is associated with a decrease in isomer shift. The isomer shifts for SnX_6^{2-} are 0.2 - 0.3 mms^{-1} less than the corresponding SnX_4 (see Table 2.2). The values for SnX_5^- (X = Cl, Br) are intermediate[13]. The decrease in isomer shift has been attributed to two factors: (i) the increasing polarity of the tin-ligand bonds which are longer for the higher coordination numbers[12,14] and (ii) the increase in shielding of the s-electrons produced by population of the tin d-orbitals.[15]

3. Structure

In organotin systems there do not appear to be any changes in the isomer shift which are attributable directly to the change in coordination number. It has been suggested that the isomer shift in organotin compounds is a function of the stereochemistry.[12] This is most clearly seen in the comparison of cis- and trans-octahedral R_2SnX_4-systems, where it is generally found that, for comparable ligands, the cis-complexes have lower isomer shifts than the trans-complexes as shown in Table 2.5.

(b) Quadrupole Splitting

In Section 2.2.2, it was mentioned that contributions to the E.F.G. may be considered to arise from (i) the electrons of the valence shell of the Mössbauer atom itself and of the bonds between it and the ligands (q_{val}) and (ii) charges on the atoms directly bonded to the Mössbauer atom (q_{lat}). It is normally assumed, on account of the inverse cubic dependence on distance, that q_{val} will be much larger than q_{lat}.[9]

In qrder to be able to correlate the magnitude of the quadrupole splitting with the geometry and electronic structure of the compound, a means of computing the relative magnitude of the E.F.G. is needed. The simplest approach to this is the point charge model which has been described by other workers.[17,21,22]

Table 2.5 Isomer Shift Data for cis- and trans-R_2SnX_4, mms^{-1} [†]

cis-R_2SnX_4	δ	trans-R_2SnX_4	δ
$Me_2Sn(oxin)_2$	0.77	$(PyH)_2[Ph_2SnCl_4]$	1.44
$Et_2Sn(oxin)_2$	0.87	$(PyH)_2[Me_2SnCl_4]$	1.59
$Ph_2Sn(oxin)_2$	0.72, 0.83	Me_2SnSO_4	1.61
$Ph_2Sn(acac)_2$	0.74	$Me_2Sn(acac)_2$	1.18
$Ph_2Sn(NCS)_2bipy$	0.82	$Bu_2Sn(NCS)_2bipy$	1.43
$Ph_2Sn(NCS)_2phen$	0.81	$Bu_2Sn(NCS)_2phen$	1.42

([†] See references 16,17,18,19,20)

The point charge model predicts that within a series of
octahedral complexes $RSnX_5$, cis-R_2SnX_4, trans-R_2SnX_4, the
quadrupole splittings are expected to be in the ratio
1 : 1:2.   Values for some compounds whose structures
have been examined independently are given in Table 2.6.
Bearing in mind the range of ligands used, the agreement
with the point charge model is good.   Similar agreement
is found for tetrahedral compounds, for which the ratio
$RSnX_3:R_2SnX_2:R_3SnX$ should be 1 : 1.15 : 1 (Table 2.7).
As might be expected, five-coordinate compounds of the
type R_3SnX_2 give intermediate values (Table 2.8).
Semi-quantitative agreement with the predictions of the
point charge model is good, and can assist in the
determination of structures.

Table 2.6   **Quadrupole Splitting Data for Octahedral**

Organotin Complexes   mms^{-1}[†]

RSnX$_5$		cis-R$_2$SnX$_4$		trans-R$_2$SnX$_4$	
PhSnCl$_5^{2-}$	1.92	Me$_2$Sn(oxin)$_2$	1.98	Me$_2$SnF$_2$	4.11
BuSnCl$_5^{2-}$	1.86	Bu$_2$Sn(oxin)$_2$	2.05–2.21	Me$_2$SnCl$_2$.2DMSO	4.16
BuSnCl$_3$Br$_2^{2-}$	1.85	Ph$_2$Sn(oxin)$_2$	1.63–1.78	Me$_2$Sn(acac)$_2$	3.93
BuSnCl$_3$2DMSO	1.73	Ph$_2$Sn(NCS)$_2$bipy	2.13	Me$_2$SnCl$_4^{2-}$	4.32
BuSnCl$_3$.2py	1.86	Ph$_2$Sn(NCS)$_2$phen	2.34	Bu$_2$Sn(NCS)$_2$bipy	4.04
BuSnCl$_3$.2Ph$_3$PO	2.32			Bu$_2$Sn(NCS)$_2$phen	4.18

([†] See references 16,17,18,19,24,25)

Table 2.7   **Quadrupole Splitting Data for Tetrahedral**

Organotin Compounds, mms^{-1}[†]

R, X	R$_2$SnX	R$_2$SnX$_2$
Me, C$_6$F$_5$	1.27	1.51
Ph, C$_6$F$_5$	0.90	1.11
Ph, C$_6$Cl$_5$	0.84	1.23
Ph, S	1.17	1.29
Me, C≡CCF$_3$	1.77	1.95
Ph, Cl	2.48	2.82
Ph, Br	2.48	2.54
Ph, I	2.09	2.38

([†] See references 26,27,28,29,30,31)

Table 2.8 Quadrupole Splitting Data for Trigonal
Bipyramidal Organotin Compounds, mms^{-1}[†]

Compound

Me_3SnF	3.86
Me_3SnOH	2.91
$Me_3SnCl.Py$	3.44
$Me_3SnCl.Imidazole$	2.76
$Me_3SnCl_2^-$	3.27
$Et_3SnCl_2^-$	3.44
$Ph_3SnCl_2^-$	3.00
$Me_3SnBr_2^-$	3.45

([†]See references 22,28,30)

2.2.4 Magnetic Hyperfine Interaction

The magnetic hyperfine splittings arise from the interaction of the nuclear dipole magnetic moment, μ, with the hyperfine field, B, existing at the nucleus. The Hamiltonian representing the interaction is given by:

$$\mathcal{H} = -\mu.B = -g_N\mu_N I.B \qquad (2.27)$$

where g_N = nuclear gyromagnetic ratio

μ_N = nuclear magneton

I = nuclear spin angular momentum.

The interaction removes the degeneracy of the nuclear spin, I, to split each level into (2I + 1) sub-levels. The shifts in the nuclear energy levels associated with the loss of degeneracy are given by:

$$E_{m_I} = -\mu_N.B_{m_I} \quad \text{(for } m_I = I, I - 1, I - 2, ..I) \quad (2.28)$$

$$E_{m_I} = -g_N\mu_N.B.m_I \qquad (2.29)$$

A useful application of this interaction is obtained using the ^{57}Fe nucleus. For ^{57}Fe the g_N differs in sign for the ground and excited states and the selection rules concerning the allowed Mössbauer transitions ($\Delta m = 0, \pm 1$) give rise to a symmetric six-line spectrum (Figure 2.8). The spacings between the line pairs (1,2), (2,3), (4,5), and (5,6) are equal since

for $I = \frac{3}{2}$, $E = -g_N\mu_N.B.\frac{3}{2}$

and for $I = \frac{1}{2}$, $E = -g_N\mu_N B.\frac{1}{2}$

hence $m = I\frac{3}{2} - I\frac{1}{2} = -g_N.\mu_N.B.$
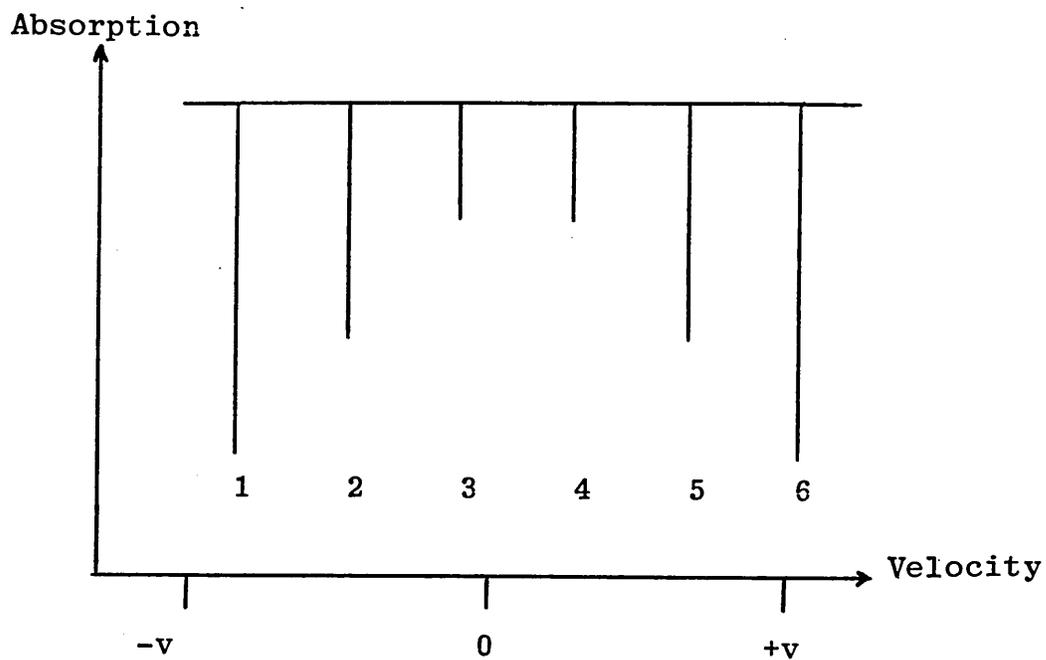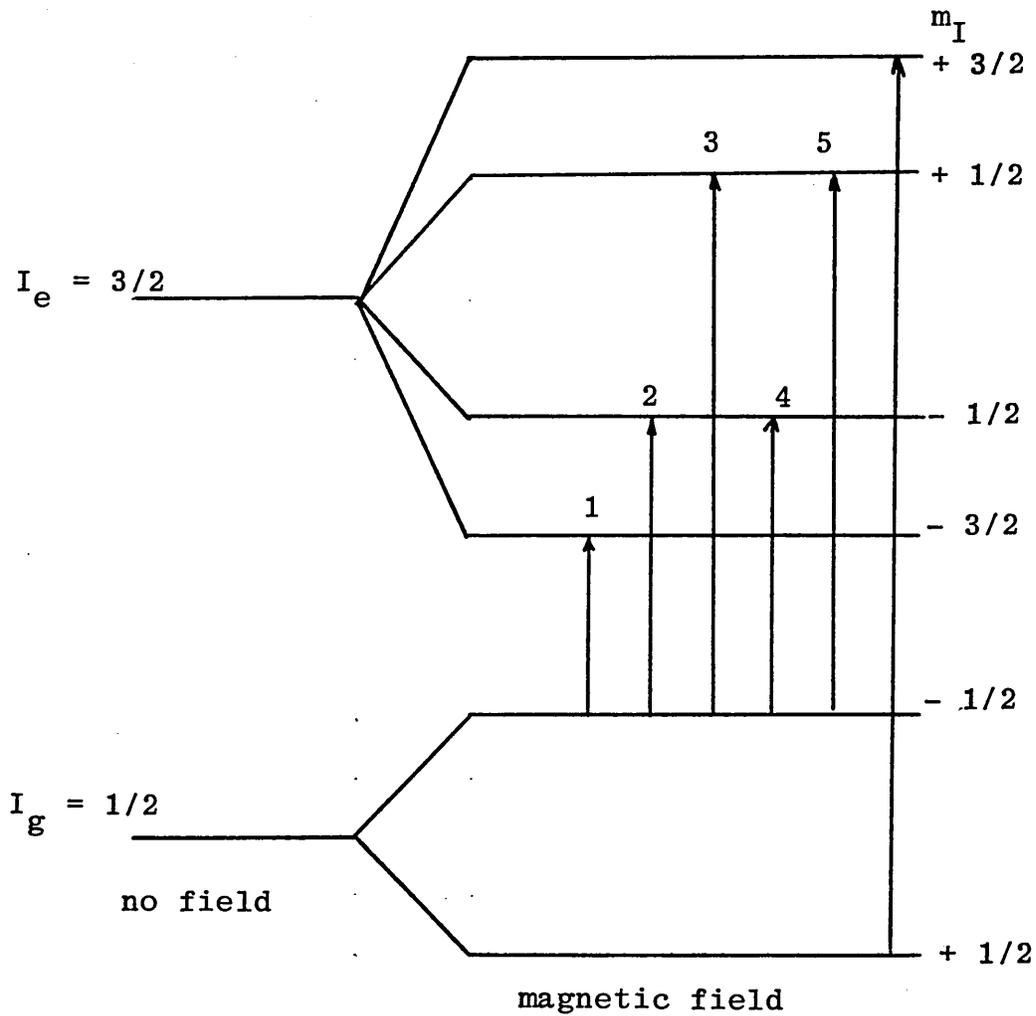
Hence the peaks are equally spaced which is useful for testing velocity linearity of the Mössbauer spectrometer. The absolute line energies and corresponding Doppler shift velocities have been determined independently by several workers using a number of absolute calibration standards. The determined values of the line positions are used as secondary standards to calibrate the spectrometer.

The line widths of the six peaks are in general equal, but the intensities are different. The line intensities are given by:

$$I_1 = I_6 = 3 \ (1 + \cos^2\theta) \qquad\qquad (2.30)$$

$$I_2 = I_5 = 4\sin^2\theta \qquad\qquad (2.31)$$

$$I_3 = I_4 = 1 + \cos^2\theta \qquad\qquad (2.32)$$

(Data from Mössbauer Effect Data Index, 1975)

Where θ is the angle relative to the principal axis of the magnetic field.

2.3 EXPERIMENTAL DETAILS

2.3.1 Characteristics of a useful Mössbauer Isotope

The great majority of Mössbauer work has used the isotopes ^{57}Fe and ^{119}Sn but there are at least thirty-three elements which show the effect. Below are listed the important criteria which make a particular isotope useful for Mössbauer research:

(i) The source must emit a suitable low energy γ-ray (< 150 keV). The magnitude of E_γ is important since the smaller E_γ the greater the recoilless fraction 'f'.

(ii) The Mössbauer γ-ray must be well resolved from other photons in order to reduce background levels.

(iii) The radioactive decay of the source must prove convenient for practical experiments (for example, the parent nuclei for Nickel Mössbauer spectroscopy are ^{61}Co and ^{61}Cu, which have half lives of 17 hours and 3.3 hours respectively, and are far too short for routine experiments).

(iv) The magnitude of the Mössbauer effect is proportional to the area under the absorption curve. In general, for a 'thin' Lorentzian absorption line, the area is given by:

$$A = \tfrac{1}{2}\pi.f_a.f_s.\sigma_0.n.X.\beta \qquad\qquad (2.33)$$

where f_a, f_s = recoilless fraction of the absorber

and source respectively

σ_0 = isotope cross-section

n = isotope natural abundance

X = absorber thickness

β = 1/number of absorption lines.

From the above expression, it is apparent that only those isotopes which have a high natural abundance, large cross-section and large recoil-free fraction will give a significant Mössbauer effect.

(v) Having chosen an isotope which gives a large Mössbauer effect and has a long parent half life, the line positions must be sensitive to the chemical environment to resolve the hyperfine interactions and have lines which are close to the natural line width.

2.3.2 The Mössbauer Source

The decay of ^{119m}Sn emits a γ-ray of energy 23.8 keV ($t_{\frac{1}{2}}$ = 245d) which has a natural line width of ω_0 = 0.6467 mms^{-1}.[32] The decay scheme for ^{119}Sn is shown in Figure 2.9(a). The source used during this investigation was a 15mCi ^{119}Sn isotope in a BaSnO$_3$ matrix. This has a full width at half height of 0.8196 mms^{-1}, measured against a 0.0125 mm tin absorber, and an isomer

Figure 2.9(a) Nuclear Decay Scheme for ^{119}Sn

^{119}Sb
_____

38h

E.C.
100%

^{119m}Sn
_____ $-11/2$
250d

γ 89.5 keV

_____ $+ 3/2$

γ 23.8 keV

_____ $+ 1/2$
^{119}Sn
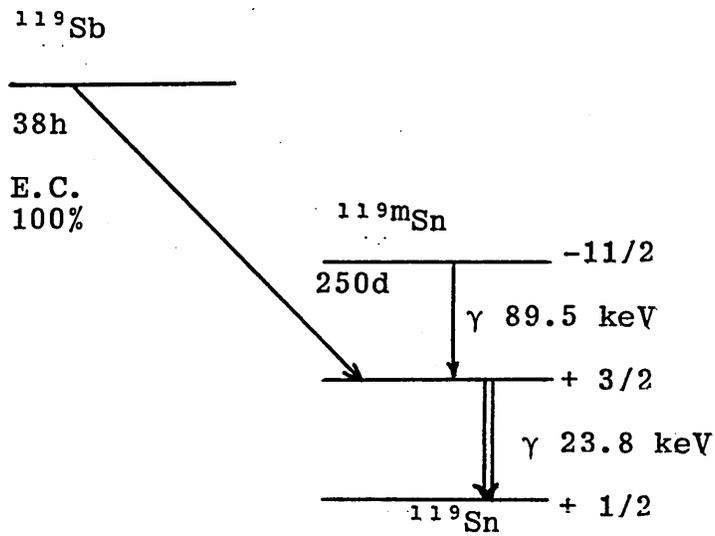
Figure 2.9(b) Nuclear Decay Scheme for ^{57}Fe

^{57}Co
_____

270d

E.C.
99.8%

_____ $-5/2$

γ γ
(136.4   (122.0
keV)   keV)

_____ $-3/2$

γ 14.4 keV

_____ $-1/2$
^{57}Fe
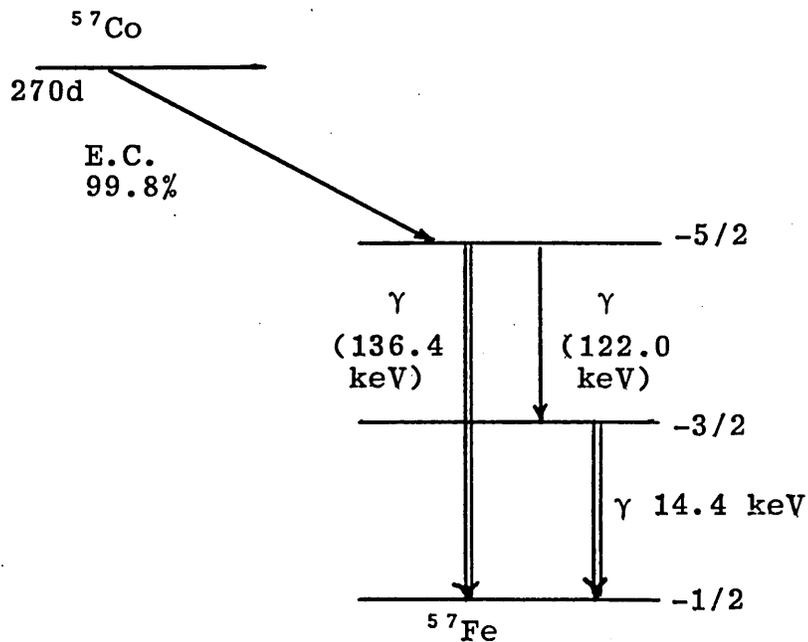
shift of +2.55 mms^{-1} corresponding to β-tin.

For the purpose of calibration and linearity checks of the spectrometer, the magnetic hyperfine splitting of the ground and first excited state of ^{57}Fe was used. To observe this the 14.4 keV γ-ray transition to the ground state of ^{57}Fe was employed which is emitted during the decay of ^{57}Co ($t_{\frac{1}{2}}$ = 270d) shown in Figure 2.9(b). The 14.4 keV γ-ray has a natural line width ω_0 = 0.1940 mms^{-1}.[32] The source used was a ^{57}Co isotope in a palladium matrix with an estimated activity of 3mCi, having a single line with a full width at half height of 0.22 mms^{-1}.

Both sources had an acceptable recoilless fraction at room temperature. Nuclear parameters for ^{119}Sn and ^{57}Fe are given in Table 2.9.

2.3.3 The Absorbers : Preparation and Method of Gamma-Irradiation

Three commercially available organotin stabilisers (supplied by Lankro Chemicals Ltd) were studied:

1. Dioctyltinbis(isooctylthioglycollate)

   $(C_8H_{17})_2Sn(SCH_2COOC_8H_{17})_2$, $Oct_2Sn(IOTG)_2$ [1]

2. Dibutyltinbis(isooctylthioglycollate)

   $(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$, $Bu_2Sn(IOTG)_2$ [2]

3. Dibutyltinbis(isooctylmaleate)

   $(C_4H_9)_2Sn(OCOCH=CHCOOC_8H_{17})_2$, $Bu_2Sn(IOM)_2$ [3]

(Data for both nuclei obtained from the Mössbauer Effect

Data Index 1975)

^{119}Sn	^{57}Fe
E_γ = 23.8 keV μ_g = -1.04621(6) nm μ_e = +0.682(8) nm R_μ = $\dfrac{\mu_e}{\mu_g}$ = -0.6519	E_γ = 14.4 keV μ_g = +0.09024(7) nm μ_e = -0.15460(16) nm R_μ = $\dfrac{\mu_e}{\mu_g}$ = -1.7132
Γ = 2.570 x 10^{-8} eV ω_0 = 0.646(4) mms^{-1} Isotopic Abundance = 8.58%	Γ = 4.665(7) x 10^{-9} eV ω_0 = 0.1940(3) mms^{-1} Isotopic Abundance = 2.14%
	Line positions (symmetrical) E 1,6 ± 5.312(4) mms^{-1} E 2,5 ± 3.076(2) mms^{-1} E 3,4 ± 0.840(2) mms^{-1}
$\dfrac{g_e}{g_g}$ = -0.2173	$\dfrac{g_e}{g_g}$ = -0.57106

Compounds [1], [2] and [3] are viscous liquids at room
temperature. In order to record their Mössbauer
spectra, these liquids were injected into a perspex
sample disk with internal dimensions 1 mmx 1.5 cm diameter
and attached to the Mössbauer sample probe head
(Figure 2.13).

Compounds [1] and [2] were incorporated into PVC at
1.2% (w/w), and 2% (w/w) for [3]. Two methods of
incorporating the stabilisers into PVC were used:-

(a) Conventional Hot Milling

An intimate mix of PVC powder (Breon S110/0 supplied by
Lankro Chemicals Ltd) and stabiliser, at the required
concentration, was continually passed between heated
rollers at 185°C to produce uniform, colourless sheets.
The contact time between the PVC mix and the rollers
was kept to a minimum in order to reduce thermal and
mechanical degradation of the PVC.[33,34]

(b) Solvent Casting

The required amount of PVC and stabiliser were dissolved
in the minimum amount of solvent (either dichloromethane
(distilled over calcium hydride) for the thioglycollate
stabilisers [1] and [2] or tetrahydrofuran (distilled
over potassium metal) for the maleate stabiliser [3]).
The polymer-stabiliser solution was poured into a shallow
dish and the solvent left to evaporate. The resulting
PVC films were dried to constant weight in a vacuum
oven at 40°C.

Moisture sensitive tin compounds such as dibutyltin dichloride, butyltin trichloride and stannic chloride were dispersed in PVC by this method, using dichloromethane. All manipulations were carried out in an air-tight glove box with phosphorus pentoxide as a precautionary drying agent. The solvent was removed from this closed system by a steady flow of nitrogen gas through the glove box.

1.5 cm diameter disks were cut from the PVC sheets and secured to the sample probe by placing them between the base of the probe and the cover plate which is attached to the probe by four brass screws.

Gamma-Irradiation of PVC Samples

The PVC samples containing the organotin stabilisers were irradiated in air by ^{60}Co gamma- radiation (Isotron Ltd, Swindon). The source used consisted of ^{60}Co tubes mounted in a circular array at the bottom of a 20 ft deep water pond. The samples were loaded into water-tight containers, lowered to the centre of the array and the exposure was accurately timed. The samples were irradiated in glass phials at a dose rate of approximately 5 kGy/hr (1 Gy = 1 J kg^{-1}) at ambient temperature. Doses in the range 1 kGy – 200 kGy were used in the course of this investigation.

Absorber 't' Values

Earlier it was shown (Section 2.1.2) that the line width of the emitted γ-ray is related to the half-life of the excited nuclear state by $\Gamma_H = h.0.693/t_{\frac{1}{2}}$. In practice, the observed line width at half maximum is influenced by the thickness of the absorber. As the thickness of the absorber increases, the line shape begins to deviate from the Lorentzian shape and saturation effects occur. An optimum practical absorber thickness is usually determined in order to observe a reasonable effect.

A quantitative appreciation of the effect of varying the absorber thickness is obtained by considering the area under the absorption curve. Brooks and Williams[35] showed that in general:

$$A(t) \propto \tfrac{1}{2}t \exp(-\tfrac{1}{2}t).[I_0(\tfrac{1}{2}t) + I_1(\tfrac{1}{2}t)] \qquad (2.34)$$

where A(t) is the area under the absorption curve arising
        from an absorber of thickness 't'
  I_0 is a Zero order Bessel function
  I_1 is a First order Bessel function.

The above expression can be reduced to a first approximation, to:

$$A(t) \propto f_s t(1 - 0.25t + 0.0625t^2 + ...) \qquad (2.35)$$

for values of $t \ll 5$. (f_s = Lamb-Mössbauer factor for recoilless fraction in the source). Where t is large ($\geqslant 10$) equation (2.34) must apply.

The absorber thickness is calculated using the equation:

$$t = \beta.n.f_a.\sigma_0.X \qquad (2.36)$$

where n = no. of resonant nuclei/cm^3

σ_0 = resonant cross-section

f_a = absorber recoilless fraction

X = actual absorber thickness

β = 1/number of absorption lines.

In practice, evaluation of the optimum absorber thickness using (2.34) is limited due to f_a being unknown for many compounds. In addition, the absorption curves are susceptible to deviations from the Lorentzian shape due to particle size effects, crystal orientation (Goldanksii-Karyagin effect) and from additional non-resonant intensities produced by the scattering of higher energy γ-rays.

Typical t values for the organotin stabilisers dispersed in PVC at 1.2% (w/w) can be estimated from (2.36) by assuming approximate f_a values:

$$t = \beta.n.f_a.\sigma_0 \qquad (2.36)'$$

where β = $\frac{1}{2}$ for a single quadrupole doublet

$f_a \approx 0.6$ (corresponding to the maximum value where $f_a = f_s$)

$\sigma_0 = 1.403 \times 10^{-18}$ cm^2

n = number of resonant atoms per cm^2

To calculate n for a typical PVC sample containing
1.2% (w/w) of dibutyltinbis(isooctylthioglycollate) [2]:

Total mass of stabiliser [2] in sample = 9.96×10^{-3} g

Mass of ^{119}Sn in the stabiliser = 1.59×10^{-4} g

Mass of ^{119}Sn/cm^2 = 6.25×10^{-5} g/cm^2

$\therefore$ Number of atoms of ^{119}Sn/cm^2 = 3.16×10^{17} atoms/cm^2

Substituting the value for n into (2.36) gives $\underline{t = 0.133}$.

This represents a $\underline{\text{maximum}}$ expected value for a recoilless fraction of 0.6. In general, organotin compounds have recoilless fractions in the range 0.06 to 0.40 at 80K.

Equation (2.35) relates the area under the absorption peaks to the absorber thickness (for t << 5):

$$A(t) \, \alpha \, f_s.t \, (1 - 0.25t + 0.0625t^2 + ...) \qquad (2.35)$$

$$A(t) \, \alpha \, f_s.t - 0.25f_s t^2 + ...$$

Substituting for t gives:

$$A(t) \, \alpha \, f_s \, (0.133 - 0.004)$$

The term $f_s t^2$ can be considered negligible and the value calculated shows the area under the absorption peak, for the PVC samples studied, to be proportional to the absorber thickness.

The nature of the sample studied determined the amount of ^{119}Sn it contained. This dictated the length of the run-time required to obtain a good quality spectrum. For neat stabiliser samples, run-times of only 4 hours

were required. For PVC samples containing undegraded
stabilisers, run-times of up to 3 days were required.
Longer run-times, of up to 5 days, were found necessary
for γ-degraded PVC samples containing mixtures of
degradation products.

2.4 INSTRUMENTATION

In comparison with other spectroscopic techniques,
the Mössbauer equipment is rather simple. A block
diagram of the system used is shown in Figure 2.10.
It consists basically of a drive mechanism to impart
a controlled Doppler velocity to the radioactive source,
a gamma-ray detector with associated amplifying and
data collecting equipment, and a data storing device
such as a multichannel analyser. The Mössbauer
spectrum being a plot of the number of gamma-ray photons
transmitted through an absorber as a function of
instantaneous relative Doppler velocity of the source
with respect to the absorber.

2.4.1 Mössbauer Drive System and Multichannel Analyser

Throughout this investigation a Canberra Industries
Series 30, 1024 channel Multichannel Analyser (M.C.A)
was used. Two modes of operation were available :
either the Time mode, in which the analyser operates
as a multichannel scaler (M.C.S.); or the Pulse Height
Analysis (P.H.A.) mode. In the time mode, the analyser
stores the total count information in each channel
through a preset time interval of 50-100 μs. At the

Figure 2.10 : Schematic of the Mössbauer System
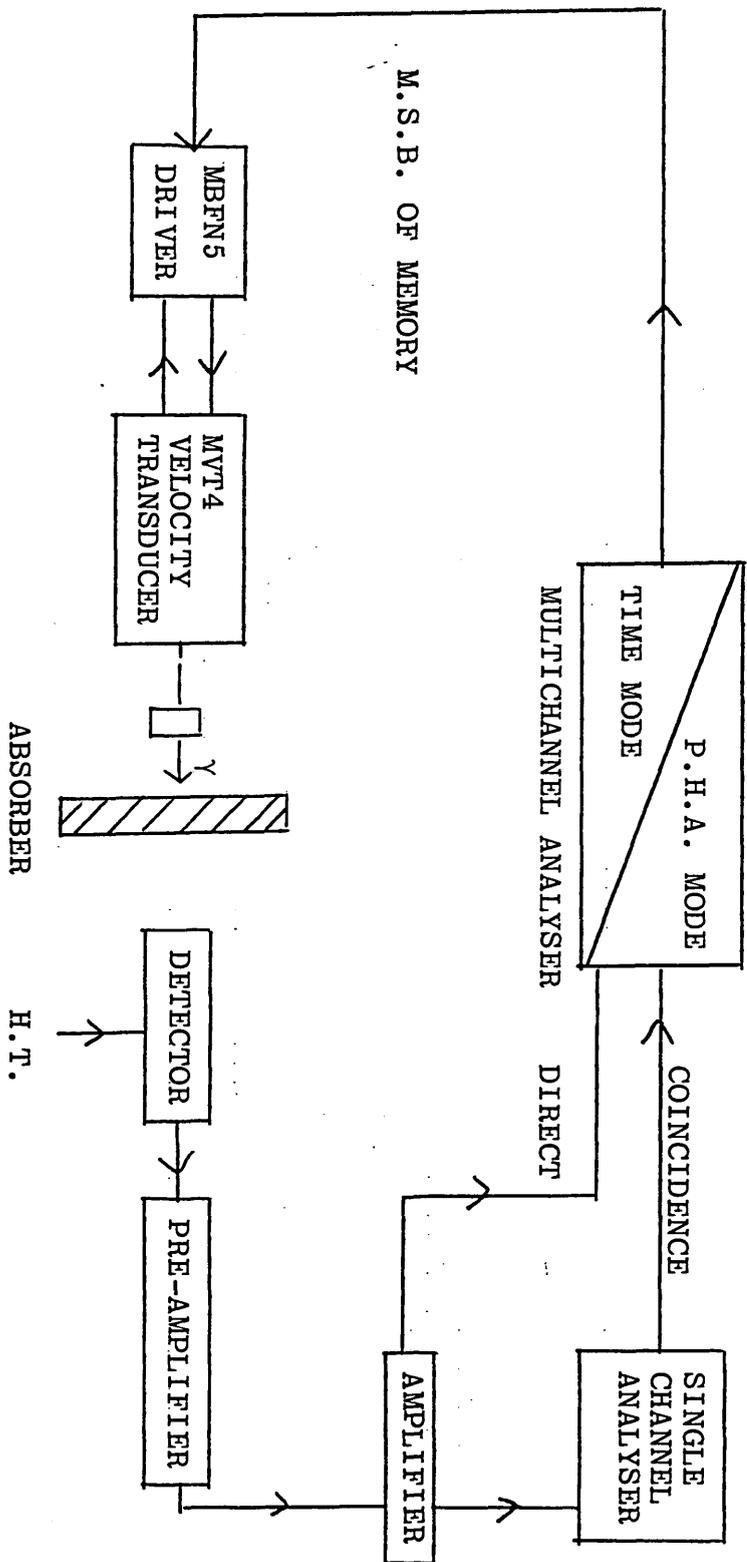
end of the time interval the address is advanced to the next sequential channel. The only dead time is that incurred during the channel advance, and is estimated to be 5-10% of the total scan time. This operating cycle is repeated over 512 channels and then recycled. When operated in the P.H.A. mode a single channel analyser is used to select the appropriate γ-ray from the source and a window can be set for the γ-ray energy of interest.

The Elscint Transducer Driving Unit, Model MDF-N-5, operated in conjunction with the Elscint Linear Velocity Transducer, Model MVT4, form the velocity servo system. This contains a wave function generator providing a sawtooth wave which operates on the M.S.B. (Most Significant Bit) of the M.C.A. The transducer driving unit imparts a linear motion to the moving rod of the transducer.

Using 512 channels of the M.C.A, a square wave is extracted from the M.S.B. of the M.C.A. such that its leading edges are at 256 and 512. This is integrated to obtain the signal representing the velocity waveform (see Figure 2.11). The transducer produces a voltage proportional to the velocity of the vibrator drive shaft. The servo amplifier compares this signal to the reference triangular waveform and applies corrections to the drive coil to minimise any differences. The amplitude of the triangular waveform determines the

Figure 2.11 : Diagram showing the Mössbauer Spectrum and related Waveforms

Channel number   0   256   512

Acceleration Waveform   −A   +A   −A

Velocity waveform   −v   0   0   t   +v   +v

Frequency = 25 Hz

'Mirror − imaged' Mössbauer spectrum   +v   0   −v   0   +v
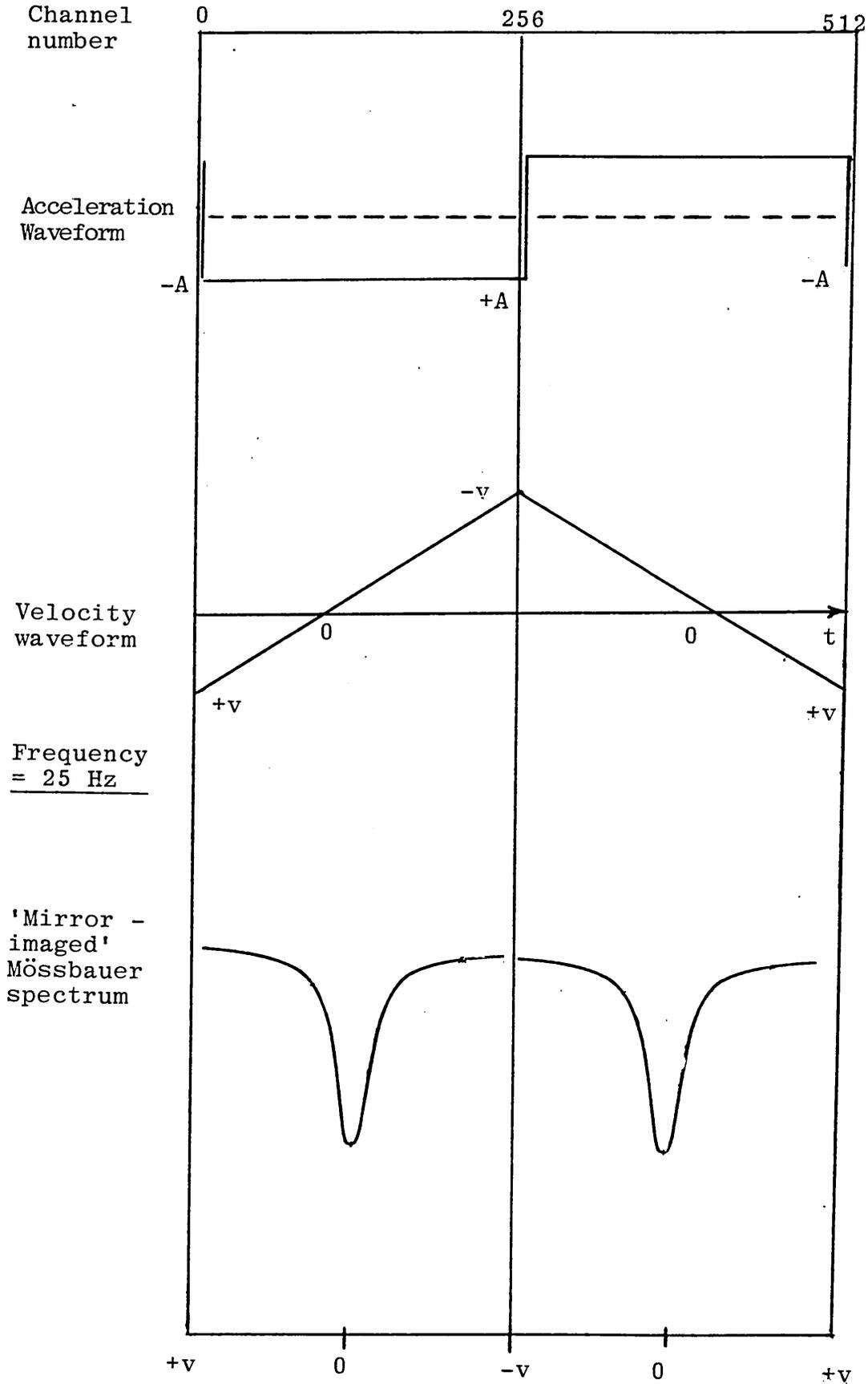
velocity range of the vibrator and can be changed using a conventional potentiometer (helipot). While the vibrator is continuously sweeping over a range of velocities, the M.C.A. is sweeping through 512 channels. The two sweeps are automatically synchronised and γ-rays from a particular velocity are fed to the same channel in the M.C.A.

Using the above symmetric waveform, a mirror image of the spectrum is obtained since, by nature of the wave-form, the velocity of the source will change from positive to negative and from negative to positive during a complete cycle.

This type of electromechanical drive has excellent long-term stability and synchronisation is ensured in a very simple manner. The velocity range needed for the isotopes studied can easily be obtained with this device, and the linearity of such systems is typically better than one per cent. The duplicate spectra obtained are useful because they can easily be folded over (mirror centre about channel 128.5) and computer averaged. Any lack of linearity in the scan will in general destroy the mirror symmetry and any spurious absorptions due to electronic faults can be recognised easily.

2.4.2 Detectors

The detection system employed consisted of either a proportional counter or a scintillation counter (depending on the energy of the γ-ray involved), a pre-amplifier and a high count-rate amplifier. Since the γ-ray transition giving rise to the Mössbauer effect in iron compounds occurs at 14.4 keV, the proportional counter is preferred as the low energy γ-rays are absorbed totally by the gas filled counter. This has better resolution and signal/noise ratio than the scintillation counter, the efficiency of which deteriorates at low energies on account of the thickness of the NaI(Tl) crystal employed. The proportional counter used contains a mixture of 90% Argon and 10% Methane providing optimum conditions for the low energy γ-ray. The operating voltage was ∿ 3 kV.

For the study of tin compounds using the 23.8 keV γ-ray energy, a sodium iodide-thalium activated, NaI (Tl), crystal scintillation counter is used since this shows much greater efficiency than the gas-filled proportional counters at energies greater than 15 keV.[36] The main advantage the solid state scintillation counter has over the proportional counter lies in the fact that the scintillation detector operates by producing electron-hole pairs as a result of the absorption of the high energy γ-ray on the NaI(Tl) crystal. The energy of the photon is rapidly transferred through a large number of electron-hole interactions to produce a large number of

low energy photons which then activate the photomultiplier. The total number of light pulses emitted by the crystal are proportional to the energy of the original γ-ray. If a gas-filled proportional counter is used to measure high energy γ-rays, the number of ions produced in the gas becomes very high and proportionality is lost and the output pulse becomes independent of the primary ionisation.

The scintillation detector used contains a 1 mm thick NaI(Tl) crystal mounted behind a thin aluminised-mylar window and was operated at a voltage of ~ 1 kV.

2.4.3   The Cryogenic System

A CF200 Oxford Instruments continuous flow cryostat was used to cool tin-containing samples to 80K before recording their Mössbauer spectra. The cryostat (Figure 2.12) contains a central chamber at its base in which a sample probe (Figure 2.13) is located. This chamber is filled with Helium exchange gas thereby eliminating the problem of cooling inherently poor thermal conductors.

Temperature control and measurement was achieved by a DTC 2 digital temperature controller and a CLTS carbon resistor located on the side of the heat exchanger as a sensor that converts temperature into an electrical signal. The signal is fed to the DTC 2 which indicates the temperature on a four digit display. The measured temperature is compared with the pre-set temperature

Figure 2.12   CF200 Continuous Flow Cryostat

Sample Access Port

Combined evacuation
and safety
valve

Transfer tube and
liquid nitrogen inlet

Sample chamber

Exchange gas space

Window
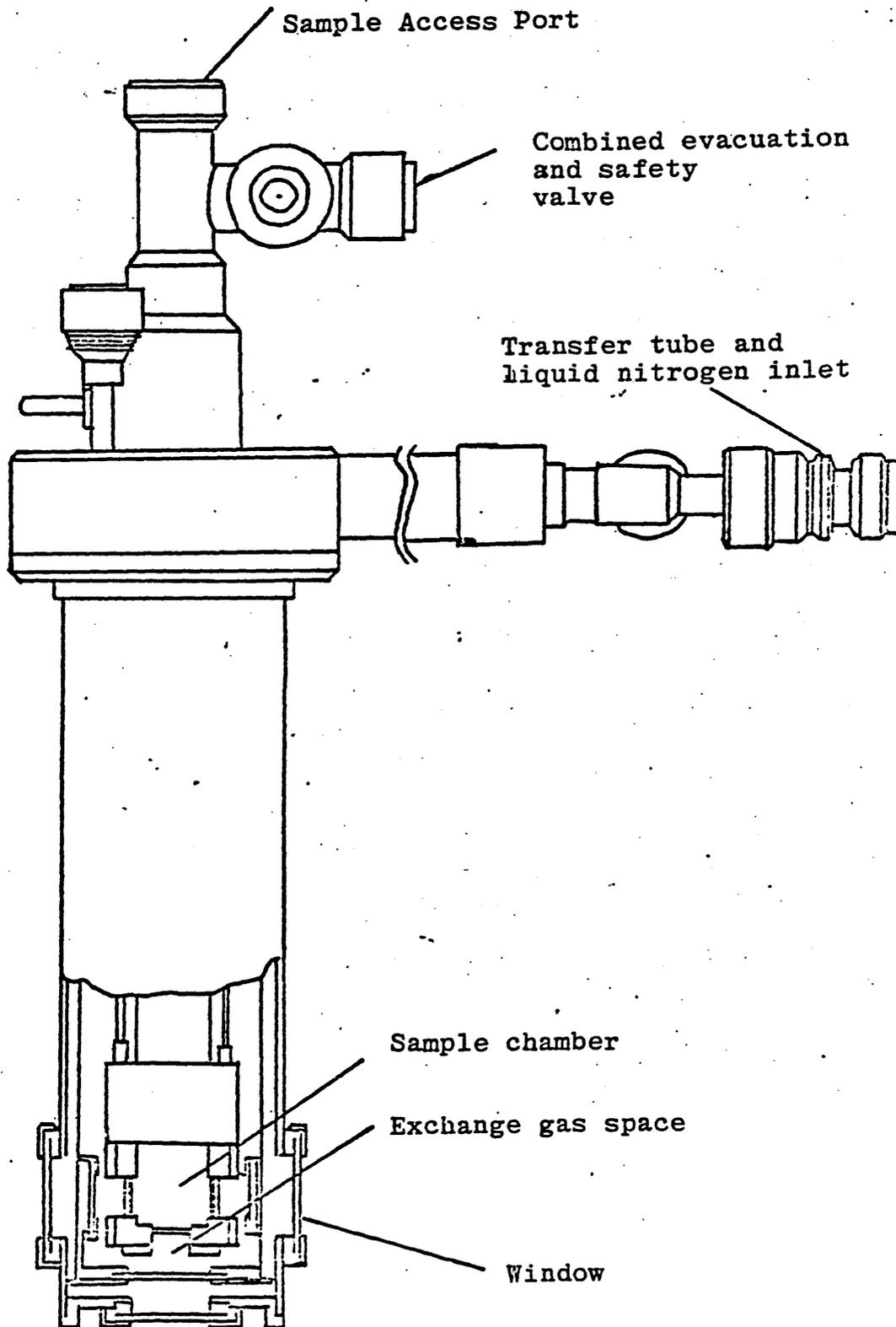
Figure 2.13 : Sample Probe for CF200 Continuous Flow
Cryostat

Carbon
resistor

Probe Head
containing sample
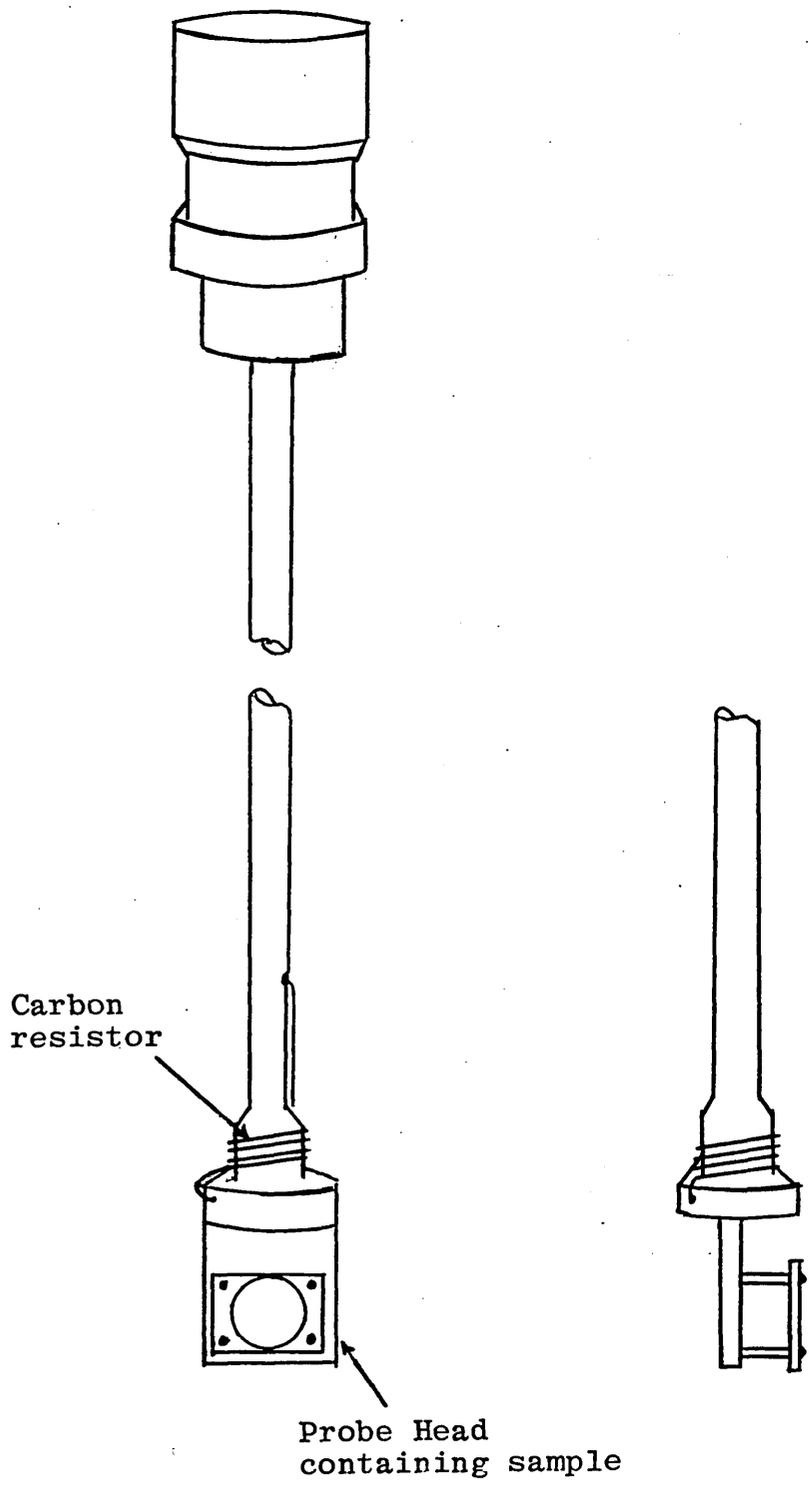
(80K) and an error signal is generated proportional to the temperature difference. The controller then regulates the amount of power fed to a heater using three term proportional differential and integral control.

Liquid nitrogen, having a boiling point of 77K, is used to obtain the temperature of 80K. The liquid nitrogen is drawn from a reservoir through a transfer tube to the outer jacket of the cryostat where it is circulated around a heat exchanger. The sample chamber, which is in good thermal contact with the heat exchanger, is first evacuated then filled with helium exchange gas to obtain efficient cooling of the sample.

The sample discs were secured to the probe by placing them between the base of the probe and a cover plate which is attached to the probe by four screws. The cover plate has a central hole which is slightly smaller in diameter than the perspex disc, used to hold the liquid samples, to allow the passage of the γ-rays to the detector. The probe is positioned in the cryostat in alignment with the aluminised-mylar windows at its base where the γ-rays enter and leave the chamber.

2.5   COMPUTER FITTING OF MÖSSBAUER SPECTRA

The use of computational facilities is essential for
the determination of line positions, line widths and
relative intensities in the Mössbauer spectra. A program
based on the work of Lang and Dale[37] on the computer
fitting of Mössbauer spectra was used for the analysis
of the data.

The constant acceleration vibrator produces a Doppler
velocity which varies from +V to 0 to -V and back to +V
through a complete cycle of 512 channels. By the nature
of the triangular waveform produced by the transducer
the two zero velocity positions are at mirror positions
and at the extremities of the source displacement.
Consequently, the spectrum produced contains the mirror
image of the data shown in the first half (0 - 255
channels) of the memory of the multichannel analyser
stored in the second half of the memory (256-511
channels).

2.5.1   Folding Program

The first operation in the fitting process is to fold
the data stored in channels 0 - 256 onto the data in
channels 256 - 512 and to add the counts stored in
the corresponding channels. An accurate determination
of the zero velocity position is ensured in the folding
process by scanning 10 half-channels either side of the
expected folding position (128.5 channels) to find the
best mirror axis for the absorption peaks so allowing

for fluctuations in D.C. levels of the drive system. The best mirror axis is determined from the sum of the square of the differences of the mirrored points.

2.5.2 Fitting Program

A visual inspection of the Mössbauer spectrum determined the type of fit to the data in the folded spectrum. The options available describing the different types of fitting conditions are listed below:

Option 1 The absorption peaks are fitted as individual lines. The computer varies the position, width and depth of each line independently to obtain the best fit.

Option 2 The absorption peaks are fitted as a number of doublets. The centre, splitting/2, widths and depths estimated from the folded data are varied until the best fit is obtained. The widths of the component lines are made equal.

Option 3 The absorption peaks are fitted as individual lines having the same widths. The computer varies the positions, widths and depths of the lines under the restriction that each line is given the same width until the best fit is obtained.

Option 4 The absorption peaks are fitted as a number of doublets but under the same restriction given in Option 3. The centres, splitting/2, widths and depths of each doublet are varied until the best fit is obtained.

Using any of these options (usually Option 1) a non-linear least squares program is used to fit the data to theoretical Lorentzian line shapes relative to a constant background which takes into account small variations from the cosine effect. This program is then used to:

(i) Calculate the line positions, widths and intensities in the spectrum from the folded data.

(ii) Calculate a minimum in the differences between the sum of the squares of the experimental data points and the theoretical data points (obtained from a second subroutine in the program). This defines the χ^2 value which has the expression:

$$\chi^2 = \sum_{i=0}^{i=255} (\chi_i^{experimental} - \chi_i^{theoretical})^2$$

If the difference between the experimental and theoretical data is large or if the amount of background scatter is great, then χ^2 will be large.

(iii) Use the least squares analysis to determine the optimum values of the background counts, baseline curvature and overall intensity of the final spectrum.

2.5.3 Calibration of the Mössbauer Spectrometer

The amplitude of the symmetric triangular waveform
which drives the vibrator, is determined by the helipot
setting on the servo amplifier and is related to the
velocity range through which the vibrator is driven.
Consequently the 512 channels containing the data must
be calibrated using the velocity range set by the
helipot relative to the amplitude of the waveform.
The calibration constant (in channels $mm^{-1}s^{-1}$) for a
particular helipot is obtained by using the magnetic
six-line spectrum of enriched iron as a calibration
standard (Figure 2.14). From Figure 2.15, it can be
seen that the data on the ascending arm of the voltage
ramp (0 - 256 channels) is the mirror image of the data
on the descending arm of the voltage ramp. The data is
thus folded thereby reducing the amount of data handled
and enabling calculation of the channel corresponding
to zero velocity (within ± 0.5 channels).

Having folded the data, the lines are fitted as pairs
i.e. (1,6), (2,5), (3,4) as described in Option 2.
Using the known Doppler velocities of the six lines
and calculated splitting/2 parameter for each pair,
the calibration constant is determined by using the
expression:

$$C = \frac{Splitting}{2 \times Doppler\ Velocity} \quad channels\ mm^{-1}\ s^{-1}$$

Figure 2.14 ^{57}Fe Mössbauer Spectrum of Enriched Iron
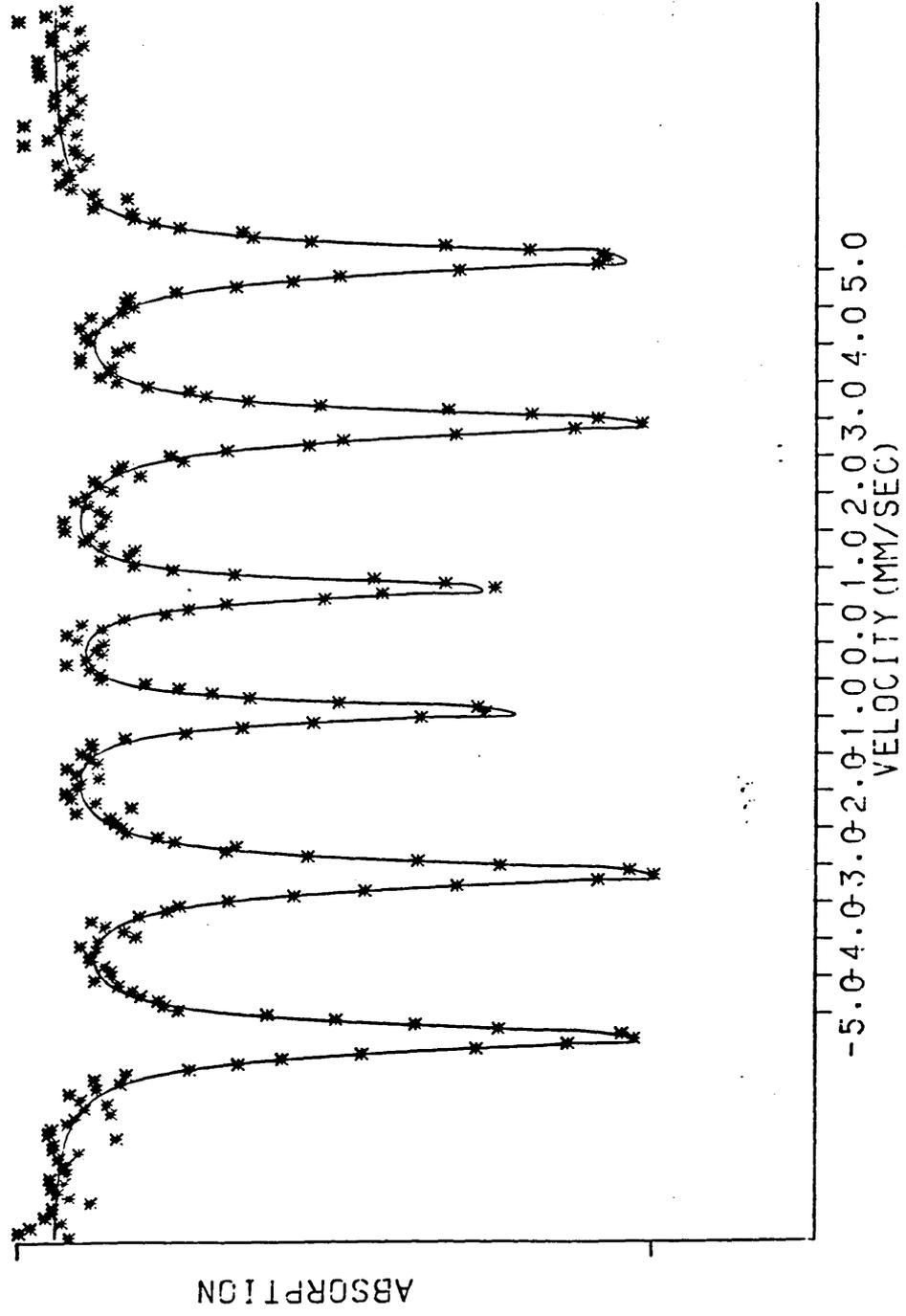
0   256   512

Channel
Number

1   2   3   4   5   6   6   5   4   3   2   1

−v   0   +v   0   −v
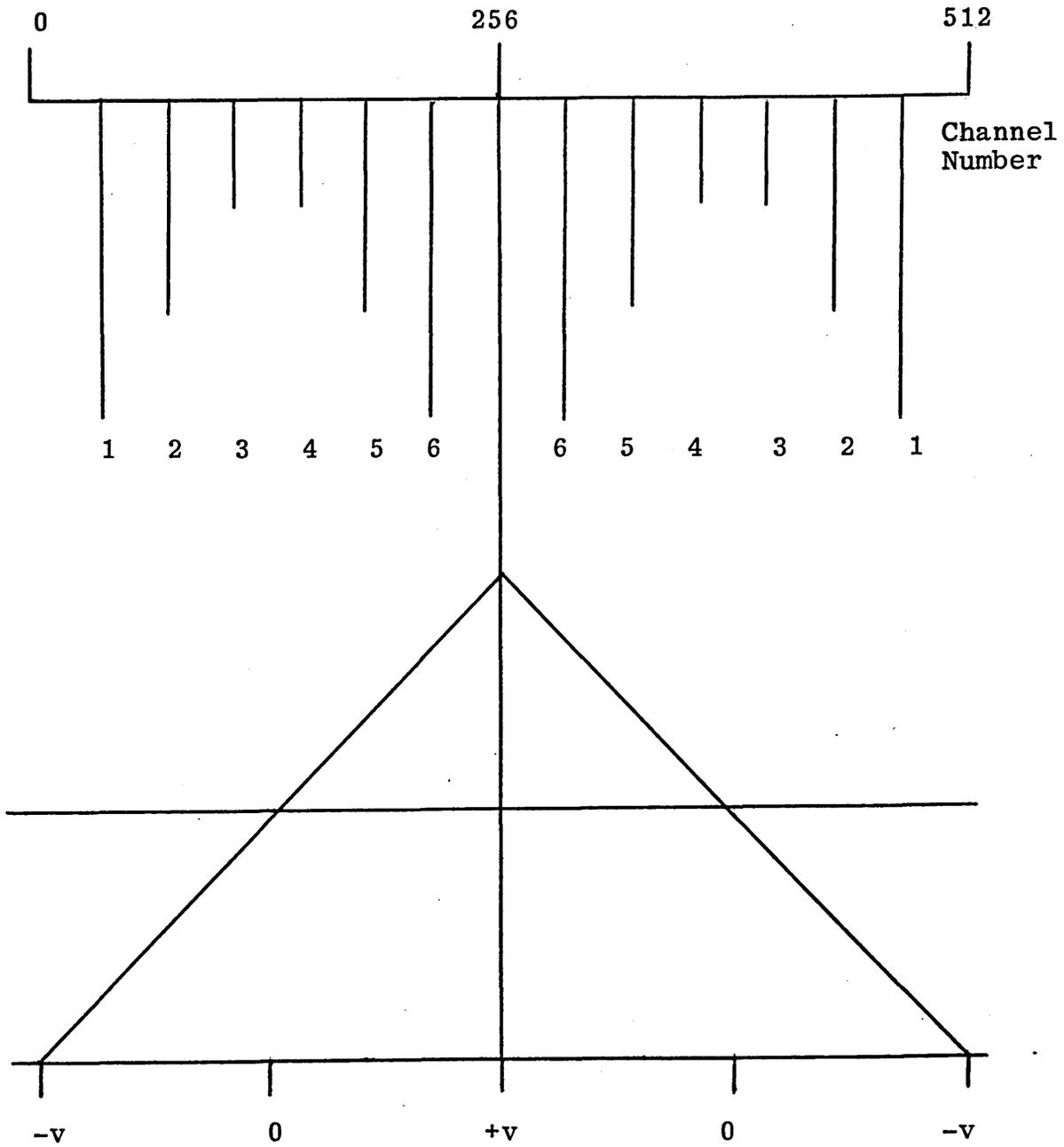
The positions of the lines are known to occur at the
following Doppler velocities:

lines $(1,6) = \pm 5.312$ mm s^{-1}

lines $(2,5) = \pm 3.076$ mm s^{-1}

lines $(3,4) = \pm 0.84$ mm s^{-1}

(line positions obtained from the Mössbauer Effect
Data Index 1975)

The final value for C is taken from the average of the
three results. Calculation of the calibration constant
over a range of velocities depends upon the helipot
being linear. The linear calibration of the helipot
was checked by measuring the calibration constant for
several helipot settings. A check on the linearity
of the triangular wave can be achieved by noting the
differences in position of the lines (in channels).

2.6 REFERENCES

1. R.L. Mössbauer, Z. Physik, 1958, 151, 124.

2. G. Breit and E. Wigner, Phys. Rev., 1936, 49, 519.

3. H.J. Lipkin, Ann. Phys., 1960, 9, 332.

4. H. Frauenfelder, 'The Mössbauer Effect',
   W.A. Benjamin, Inc., N.Y., 1962.

5. W.E. Lamb, Jr. Phys. Rev., 1939, 55, 190.

6. N.N. Greenwood and T.C. Gibb, 'Mössbauer Spectroscopy',
   1971, Chapman and Hall.

7. G.M. Bancroft, Mössbauer Spectroscopy, 1973, McGraw-
   Hill.

8. G.K. Shenoy and F.E. Wagner, Mössbauer Isomer Shifts,
   North Holland, 1978.

9. M. Cordey Hays, in Chemical Applications of Mössbauer
   Spectroscopy, V.I. Goldanskii and R.H. Herber, Eds.,
   Academic Press, New York and London, 1968, p 134.

10. R.H. Herber and H.S. Cheng, Inorg. Chem., 1970, 9,
    1686; 1969, 8, 2145.

11. A. Yu Aleksandrov, O. Yu Okhlobystin, L.S. Polak,
    and V.S. Shpinel, Dokl. Akad. Nauk. SSSR, Phys. Chem.
    Sect., 1964, 157, 768.

12. R.V. Parish and R.H. Platt, Inorg. Chim. Acta., 1970,
    4, 589.

13. K.M. Harmon, L.L. Hessel, L.P. Kleman, C.W. Kocher,
    S.V. McKinley, and A.E. Young, <u>Inorg. Chem.</u>, 1969,
    <u>8</u>, 1054.

14. J. Philip, M.A. Mullins and C. Curran, <u>Inorg. Chem.</u>,
    1968, <u>7</u>, 1895.

15. V.S. Shpinel, V.A. Bryukhanov, V. Kothekar,
    B.Z. Iofa, and S.I. Semenov, <u>Discussions Faraday Soc.</u>,
    1967, <u>1</u>, 69.

16. K.M. Ali, D. Cunningham, M.J. Frazer, J.D. Donaldson,
    and B.J. Senior, <u>J. Chem. Soc.</u>, A, 1969, 2836.

17. B.W. Fitzsimmons, N.J. Seeley, and A.W. Smith,
    <u>J. Chem. Soc.</u>, A, 1969, 143.

18. R.H. Herber, <u>Tech. Rept. 50, Int. Atomic Energy
    Agency</u>, Vienna, 1966, p 127.

19. M.A. Mullins and C. Curran, <u>Inorg. Chem.</u>, 1968, <u>7</u>,
    2584.

20. P.A. Yeats, J.R. Sams and F. Aubke, <u>Inorg. Chem.</u>,
    1970, <u>9</u>, 740.

21. R.L. Collins and J.C. Travis, in <u>Mössbauer Effect
    Methodology</u>, I.J. Gruverman, Ed., Plenum Press,
    New York, 1967, p 123.

22. R.V. Parish and R.H. Platt, <u>Inorg. Chim. Acta.</u>,
    1970, <u>4</u>, 65.

23. G.M. Bancroft, M.J. Mays and B.E. Prater, J. Chem. Soc., A, 1970, 956.

24. A.G. Davis, L. Smith and P.J. Smith, J. Organometal. Chem., 1970, 23, 135.

25. N.W.G. Debye, E. Rosenberg and J.J. Zuckerman, J. Amer. Chem. Soc., 1968, 90, 3234.

26. W.R. Cullen, J.R. Sams and M.C. Waldman, Inorg. Chem., 1970, 9, 1682.

27. V.I. Goldanksii, V.V. Khrapov, and R.A. Stukan, Organometal. Chem. Rev., A4, 1969, 225.

28. R.H. Herber, H.A. Stöcker, and W.T. Reichle, J. Chem. Phys., 1965, 42, 2447.

29. R.V. Parish and R.H. Platt, J. Chem. Soc., A, 1969, 2145.

30. P.J. Smith, Organometal. Chem. Rev., A5, 1970, 373.

31. H.A. Stöckler and H. Sano, Trans. Faraday Soc., 1968, 64, 577.

32. J.G. Stevens and V.E. Stevens, Mössbauer Effect Data Index, 1975.

33. B.B. Cooray and G. Scott, Polym. Deg. and Stab., 1980, 2, 35.

34. B.B. Cooray and G. Scott, Eur. Polym. J., 1972, 16, 169.

35. J.M. Williams and J.S. Brooks, <u>Nucl. Instr. Meth.</u>,
     1975, <u>128</u>, 363.

36. W.J. Price, <u>Nuclear Radiation Detection</u>,
     McGraw-Hill, 1972.

37. G. Lang and B.W. Dale, <u>Nucl. Instr. Meth.</u>, 1974,
     <u>116</u>, 567.

CHAPTER 3 : INITIAL IRRADIATION EXPERIMENTS

3.1   INTRODUCTION

3.2   RESULTS AND DISCUSSION

3.2.1   IDENTIFICATION OF THE TERMINAL DEGRADATION
        PRODUCT

3.3   CONCLUSIONS

3.4   REFERENCES

3.1 INTRODUCTION

The use of organotin stabilisers as thermal and photochemical stabilisers in PVC has been extensively studied (Sections 1.3 and 1.4) but there has been little work carried out on the effect of γ-irradiation on such systems when used as food packaging materials.[1,2] Maximum doses of the order 100 kGy will be applied to polymer-packaged foodstuffs[3], so the fate of organotin stabilisers in the PVC subjected to irradiation must be studied to determine the nature of the degradation process for both the polymer and stabiliser. It may then be possible to establish the likely migration products from the packaging material into foodstuffs and determine possible toxicological effects caused by the migration of these compounds. This objective has become important in view of a recent report[2] in which organotin compounds were shown to be effective at preventing discolouration and dehydrochlorination in PVC, intended for food contact packaging, during γ-irradiation.

The compounds studied in this work are dioctyltinbis-(isooctylthioglycollate), $Oct_2Sn(IOTG)_2$ [1], dibutyltinbis(isooctylthioglycollate), $Bu_2Sn(IOTG)_2$ [2] and dibutyltinbis(isooctylmaleate), $Bu_2Sn(IOM)_2$ [3]. The thioglycollate stabilisers are the most efficient stabilisers against thermal degradation whilst the maleate stabiliser is known to be an efficient photochemical stabiliser.

The stabilisers were dispersed in PVC at commercial levels[4] (1.2% by weight of polymer for the thioglycollate stabilisers and 2% by weight of polymer for the maleate stabiliser). Two methods of incorporating the stabilisers into PVC were used. The first was by hot milling, which is a common industrial method, and secondly by solvent casting which could be carried out in the laboratory. Some degradation of the stabiliser and PVC is thought to occur during the milling technique (normally carried out at temperatures in excess of 180°C[5]). This may influence the subsequent irradiation degradation process of the PVC and stabiliser. The conditions to which PVC is subjected during processing differ from those involved during thermal degradation in two respects. Firstly, mechanochemical chain-scission of the polymer under the influence of shear in the mixing process gives rise to free radicals which initiate the loss of hydrogen chloride;[6-9] secondly, the presence of oxygen, which can also react with the mechanochemically formed radicals to give hydroperoxides. The presence of hydrogen chloride, unsaturation and hydroperoxides determine the subsequent reactions of the polymer during processing, under conditions of thermal oxidation and during photodegradation[5] and may influence the effect of the irradiation degradation process of the organotin-stabilised PVC. A primary function of the alkyltin stabilisers is to neutralise hydrogen chloride and to remove unsaturation, and therefore the role of the stabiliser critically depends on the conditions to which

the polymer is subjected during processing,[10,11]
Therefore the technique of solvent casting, as a method
of sample preparation, was useful for observing the
effects of the milling operation on the performance of
the PVC samples during irradiation since these are
effectively 'unstressed' samples.

3.2   RESULTS AND DISCUSSION

The Mössbauer parameters were recorded for 1) the pure
stabilisers, 2) for the stabilisers dispersed in PVC
by milling and solvent casting, and 3) after
γ-irradiation of the PVC.   The   parameters obtained
for each of the stabilisers [1], [2] and [3] are shown
in Tables 3.1, 3.2 and 3.3 respectively.   Table 3.4
shows the parameters for compounds, in their pure state
and when dispersed in PVC, which could arise as
degradation products from stabilisers [1], [2] and [3]
after thermal degradation of organotin-stabilised PVC
systems as predicted by Frye et al.[13]

Initially, it was important that any interaction which
occurred between the stabilisers and the polymer, which
may influence the Mössbauer parameters, should be clearly
understood.   Therefore, after exposure to γ-irradiation,
any changes in the parameters from those observed prior
to irradiation of the PVC could be attributed to the
irradiation process alone.

Table 3.1 : ^{119}Sn Mössbauer Parameters for Dioctyltinbis(isooctylthioglycollate) in PVC

(at 1.2% (w/w)) at 80K

Sample	Exposure Dose kGy	δ(mms^{-1})	Δ(mms^{-1})	Γ(mms^{-1})	Relative Concentration of Components A and B (%)
Oct$_2$Sn(IOTG)$_2$ Pure	-	1.45	2.34	0.89	-
Oct$_2$Sn(IOTG)$_2$ in PVC (milled)	0	1.45	2.28	1.00	-
Oct$_2$Sn(IOTG)$_2$ in PVC (solvent cast)	0	1.43	2.43	1.16	-
Oct$_2$Sn(IOTG)$_2$ in PVC (milled)	100	0.34	-	1.06	-
Oct$_2$Sn(IOTG)$_2$ in PVC (milled)	200	0.40	-	1.16	-
Oct$_2$Sn(IOTG)$_2$ in PVC (solvent cast)	100	A 0.36 B 1.64	- 2.62	1.02 1.13	70 30
Oct$_2$Sn(IOTG)$_2$ in PVC (solvent cast)	200	0.32	-	1.16	-

Parameters ± 0.02 mms^{-1} for pure materials and ± 0.05 mms^{-1} when dispersed in PVC

Table 3.2 : ^{119} Sn Mössbauer Parameters for Dibutyltinbis(isooctylthioglycollate) in PVC

(at 1.2% (w/w)) at 80K

Sample	Exposure Dose kGy	δ(mms⁻¹)	Δ(mms⁻¹)	Γ(mms⁻¹)	Relative Concentration of Components A and B (%)
Bu₂Sn(IOTG)₂ Pure	-	1.45	2.29	0.89	-
Bu₂Sn(IOTG)₂ in PVC (milled)	0	1.48	2.30	0.95	-
Bu₂Sn(IOTG)₂ in PVC (solvent cast)	0	1.44	2.42	1.13	-
Bu₂Sn(IOTG)₂ in PVC (milled)	100	0.38	-	1.38	-
Bu₂Sn(IOTG)₂ in PVC (milled)	200	0.41	-	1.02	-
Bu₂Sn(IOTG)₂ in PVC (solvent cast)	100	A 0.34 B 1.50	- 2.61	1.04 1.08	70 30
Bu₂Sn(IOTG)₂ in PVC (solvent cast)	200	0.36	-	1.02	-

Parameters ± 0.02 mms⁻¹ for pure materials and ± 0.05 mms⁻¹ when dispersed in PVC

Table 3.3 : ^{119}Sn Mössbauer Parameters for Dibutyltinbis(isooctylmaleate) in PVC (at 2% (w/w)) at 80K

Sample	Exposure Dose kGy	δ(mms⁻¹)	Δ(mms⁻¹)	Γ(mms⁻¹)	Relative Concentration of Components A and B (%)
Bu₂Sn(IOM)₂ Pure	–	1.44	3.66	1.06	–
Bu₂Sn(IOM)₂ in PVC (milled)	0	1.40	3.38	0.88	–
Bu₂Sn(IOM)₂ in PVC (solvent cast)	0	1.36	3.34	0.98	–
Bu₂Sn(IOM)₂ in PVC (milled)	100	A 0.39 B 1.46	– 2.69	1.14 1.09	60 40
Bu₂Sn(IOM)₂ in PVC (milled)	200	A 0.41 B 1.40	– 2.50	1.08 1.08	80 20
Bu₂Sn(IOM)₂ in PVC (solvent cast)	100	A 0.37 B 1.50	– 2.82	0.95 1.12	20 80
Bu₂Sn(IOM)₂ in PVC (solvent cast)	200	A 0.40 B 1.49	– 2.62	0.86 0.94	40 60

Parameters ± 0.02 mms⁻¹ for pure materials and ± 0.05 mms⁻¹ when dispersed in PVC

Table 3.4 : ^{119}Sn Mössbauer Parameters of Compounds of General Formula R_2SnY_2 and R_2SnClY (R = Bu or Oct; Y = isooctylthioglycollate, isooctylmaleate) in the pure state or dispersed in PVC at 80K

Sample	$\delta(mms^{-1})$	$\Delta(mms^{-1})$	$\Gamma(mms^{-1})$
Oct$_2$SnCl(IOTG) Pure	1.46	2.96	1.02
Bu$_2$SnCl(IOTG) Pure	1.44	2.88	0.94
Bu$_2$SnCl(IOM) Pure	1.50	3.61	1.09
1.2% (w/w) Oct$_2$SnCl(IOTG) in PVC (milled)	1.46	2.97	1.02
1.2% (w/w) Bu$_2$SnCl(IOTG) in PVC (milled)	1.43	2.85	0.95
2% (w/w) Bu$_2$SnCl(IOM) in PVC (solvent cast from tetrahydrofuran)	1.40	3.34	0.89
Bu$_2$SnCl$_2$ Pure	1.64	3.47	0.97
1.2% (w/w) Bu$_2$SnCl$_2$ in PVC (solvent cast from dichloromethane)	1.50	3.02	0.94
Oct$_2$SnCl$_2$ Pure	1.70	3.65	0.82
1.2% (w/w) Oct$_2$SnCl$_2$ in PVC (solvent cast from dichloromethane)	1.51	3.03	0.86

Parameters ± 0.02 mms^{-1} for pure materials and ± 0.05 mms^{-1} when dispersed in PVC

A comparison of the Mössbauer data for dioctyltinbis(isooctylthioglycollate) [1] (ΔE_Q = 2.28 mms^{-1}) dispersed in PVC by milling with that for the pure stabiliser (ΔE_Q = 2.34 mms^{-1}) shows a small change in quadrupole splitting which could be attributed to some stabiliser degradation during the initial milling process. This could result in the formation of a small amount of the dioctylchlorotin thioglycollate [4] and dioctyltin dichloride.[12] The quadrupole splitting for the solvent cast sample containing the stabiliser [1] (ΔE_Q = 2.43 mms^{-1}) is slightly higher than for the pure stabiliser. This increase is difficult to explain but could be due to a weak coordinative interaction of the residual dichloromethane to the tin atom or alternatively a weak coordinative interaction between the chlorine atoms of the PVC and the tin atom may occur, as suggested by other workers.[13] Since only a small change in the quadrupole splitting occurs, it may be assumed that no significant structural change has arisen. Similar changes in parameters were observed for dibutyltinbis(isooctylthio-glycollate) [2] when dispersed in PVC by milling and solvent casting. It can therefore be assumed that the thioglycollate stabilisers [1] and [2] can be dispersed in PVC without significant degradation or structural modification. Figure 3.1 shows the Mössbauer spectra of dibutyltinbis(isooctylthioglycollate) [2] in (A) its pure state and (B) in PVC after milling, showing almost identical quadrupole doublets.

Figure 3.1.A ^{119}Sn Mössbauer Spectrum of Pure Dibutyltinbis(isooctylthioglycollate) recorded at 80k
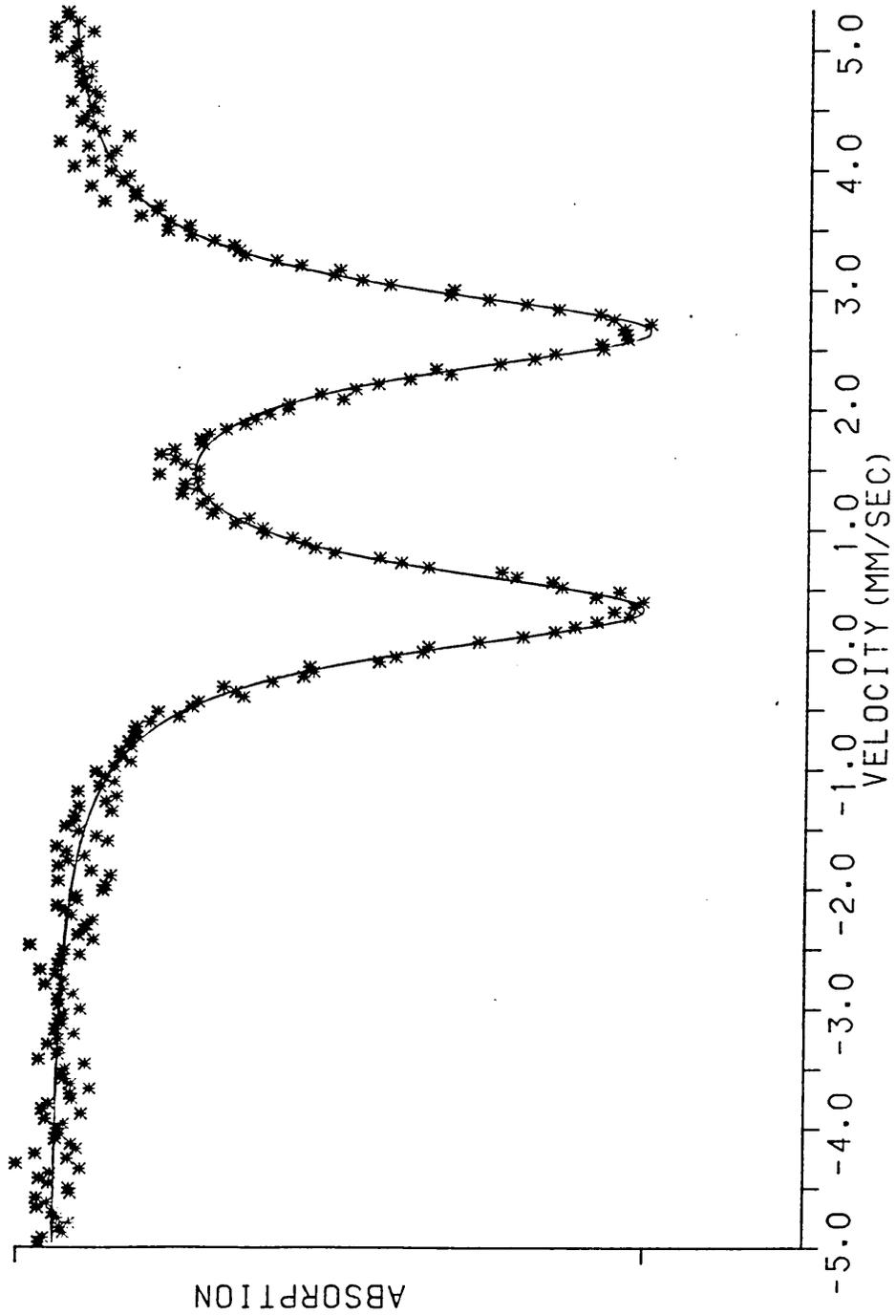
Figure 3.1.B ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in

PVC (milled) recorded at 80K

ABSORPTION

VELOCITY (MM/SEC)
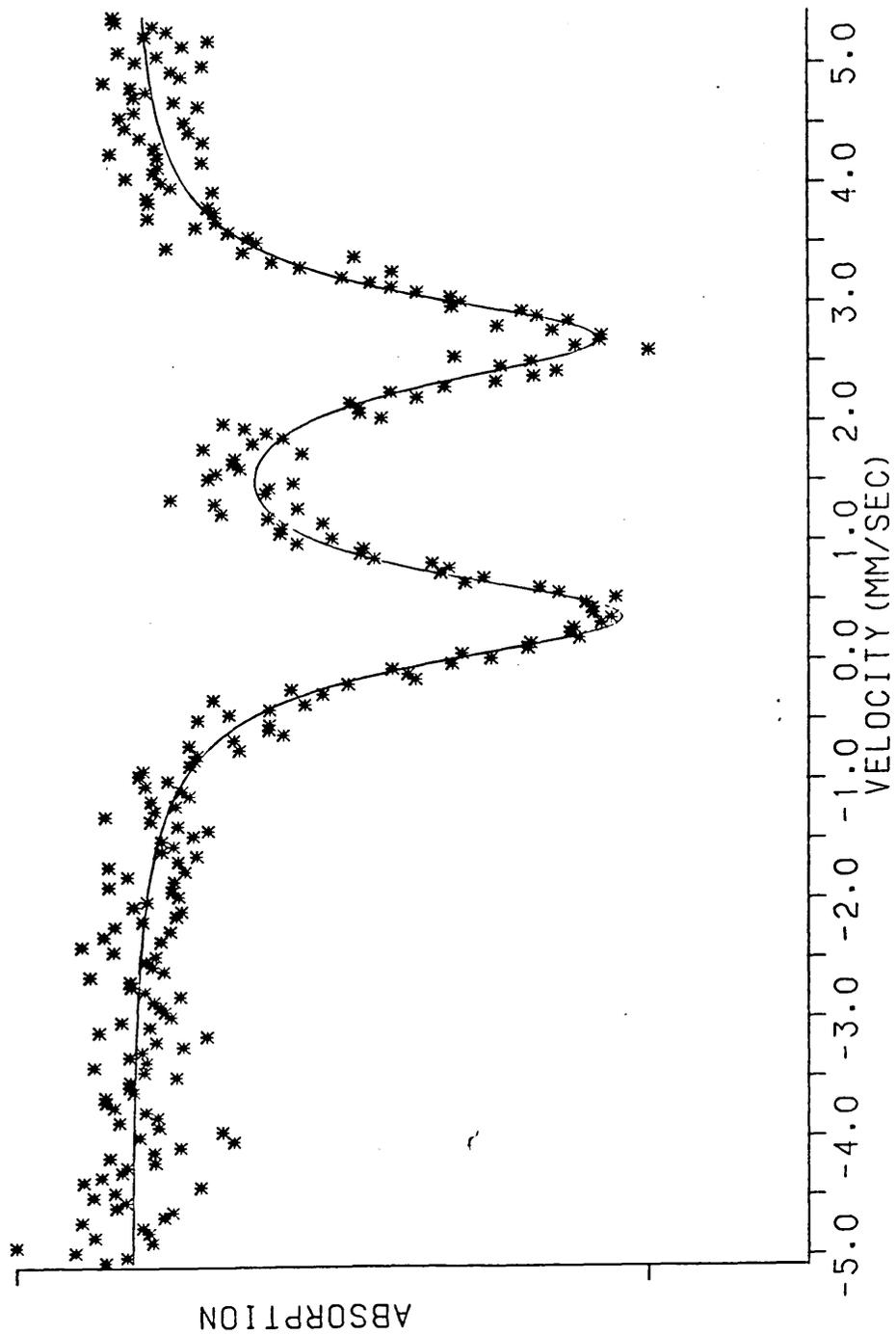
For the maleate stabiliser dibutyltinbis(isooctylmaleate) [3], a significant change in quadrupole splitting occurs from that of the pure stabiliser (ΔE_Q = 3.66 mms^{-1}) upon dispersion in PVC by either milling or solvent casting from tetrahydrofuran (ΔE_Q = 3.38 and 3.34 mms^{-1} respectively). The close similarity of the quadrupole splitting for both types of sample suggests that degradation of the stabiliser has not occurred but rather that dispersion in the PVC influences the mode of coordination of the ligands about the tin-atom. The quadrupole splitting value of the pure stabiliser [3] is typical of a six-coordinate tin site in a trans-octahedral structure (structure (a)):

(a)

[3]   ($\nu_{c=o}$ =1740cm^{-1}, 1660cm^{-1})
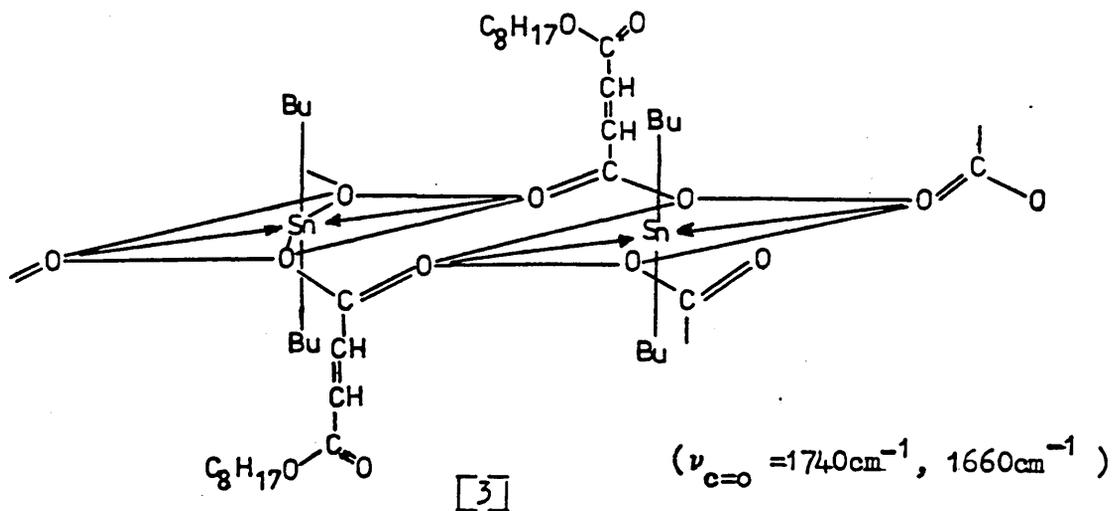
Infrared data shows both uncoordinated ($\nu_{C=O} = 1740$ cm^{-1}) and coordinated ($\nu_{C=O} = 1660$ cm^{-1}) bands present. Studies of dialkyltin acetylacetates and oxinates show similar quadrupole splitting values and these have similarly been assigned trans-octahedral structures.[14-16]

However, the magnitude of the quadrupole splitting when dispersed in PVC for the stabiliser [3] is still typical of a six-coordinated tin atom and the change in quadrupole splitting may reflect the rearrangement of O-Sn-O bonds in the formation of an intramolecular un-associated complex (structure (b)):

$$C_8H_{17}O-\overset{\overset{O}{\|}}{C}CH=CH-C \quad \overset{Bu}{\underset{Bu}{\mid}} Sn \quad C-CH=CHC-OC_8H_{17}$$

(b)
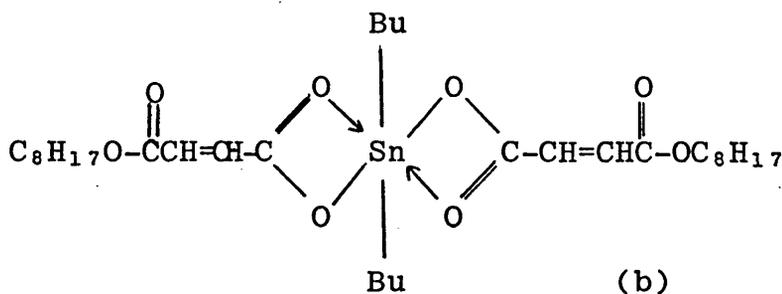
[3]

Structural changes of this type have been observed by Honnick and Zuckerman,[17] for diorganotin halide carboxylates, and suggest that the origin of certain changes in infrared spectroscopic properties, in passing from the pure compound to a solution in an inert solvent, might be attributed to a change from a polymeric penta-coordinated structure (structure c) to a monomeric penta-coordinated structure (structure d).

R   R   R   R   X
 \   /   \ /   R |
  Sn —— O   O — Sn — O   O—   \ Sn — O
  | | / | |
  X   X   R O — C
  | | \
  C   C   R'
  | |
  R'   R'
 (c)   (d)
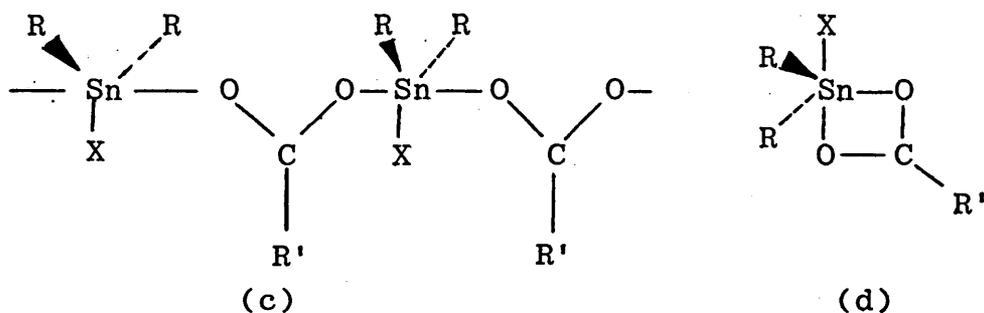
Upon irradiation of the PVC samples, severe discolouration occurs after an exposure of 100 kGy, the milled PVC samples appearing black in colour while the solvent cast samples become severely yellowed but remain transparent. The thioglycollate stabilisers [1] and [2] appear to behave in a similar manner after an exposure of 100 kGy (Tables 3.1 and 3.2 respectively).

The spectra of the milled PVC samples, for stabilisers [1] and [2], are dominated by an intense single line (δ=0.34 and 0.38 mms^{-1} respectively) and no other lines are clearly visible. Exposure of milled samples to a dose of 200 kGy results in an increase in velocity of these lines. (δ = 0.40 and 0.41 mms^{-1} respectively). Figure 3.2 shows the Mössbauer spectra of dibutyltinbis (isooctylthioglycollate) [2] in (A) milled PVC after an exposure of 100 kGy and (B) in milled PVC after an exposure of 200 kGy. The observed increase in the line position for this product on increasing the exposure to 200 kGy may not result from the conversion of this species to another but may reflect the insensitivity of the

Figure 3.2.A ¹¹⁹Sn Mössbauer Spectrum of Dibutyltinbis(isoctylthioglycollate) in

PVC (milled) after an Exposure of 100 kGy recorded at 80K
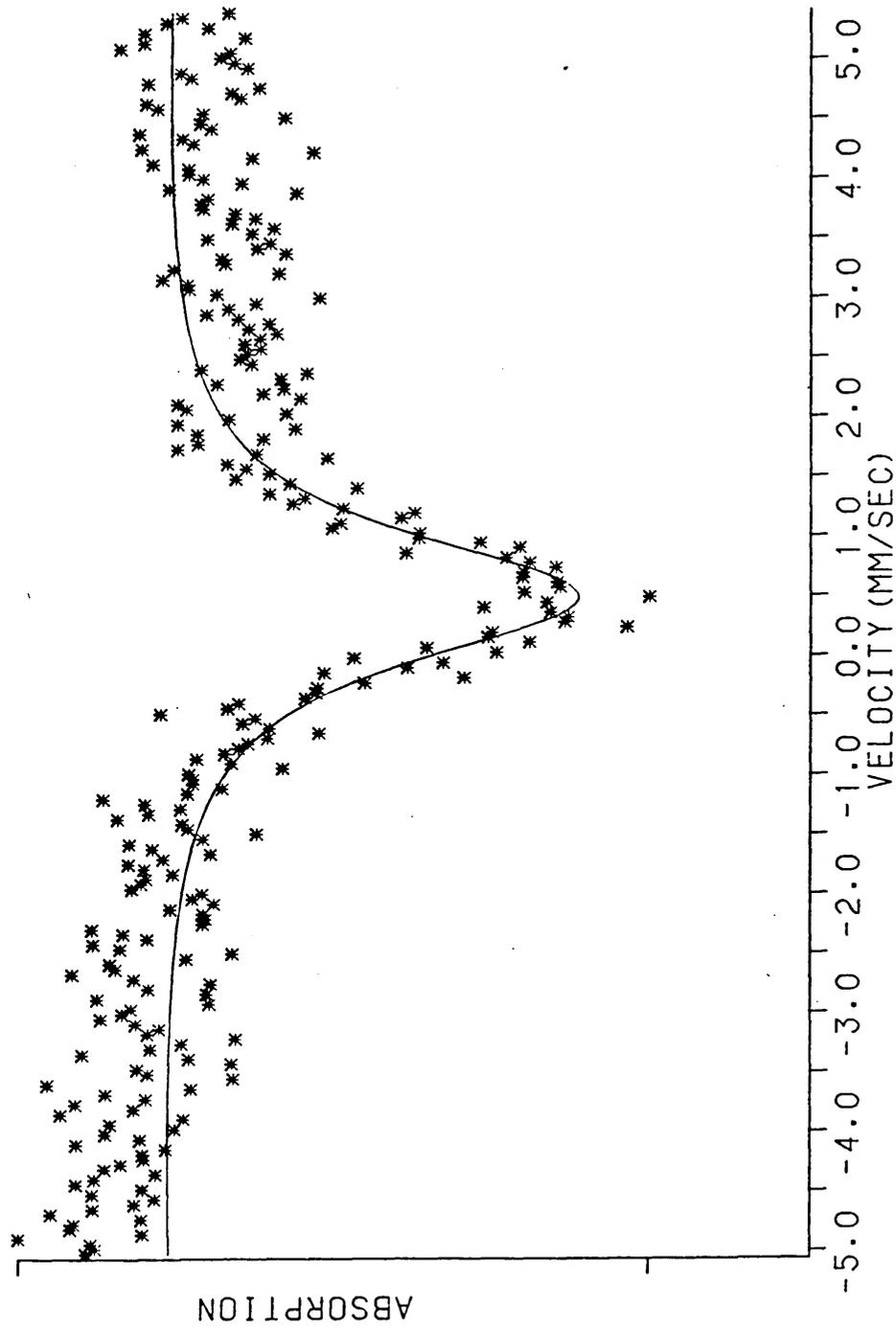
Figure 3.2.B ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC (milled) after an Exposure 0f 200 kGy recorded at 80K
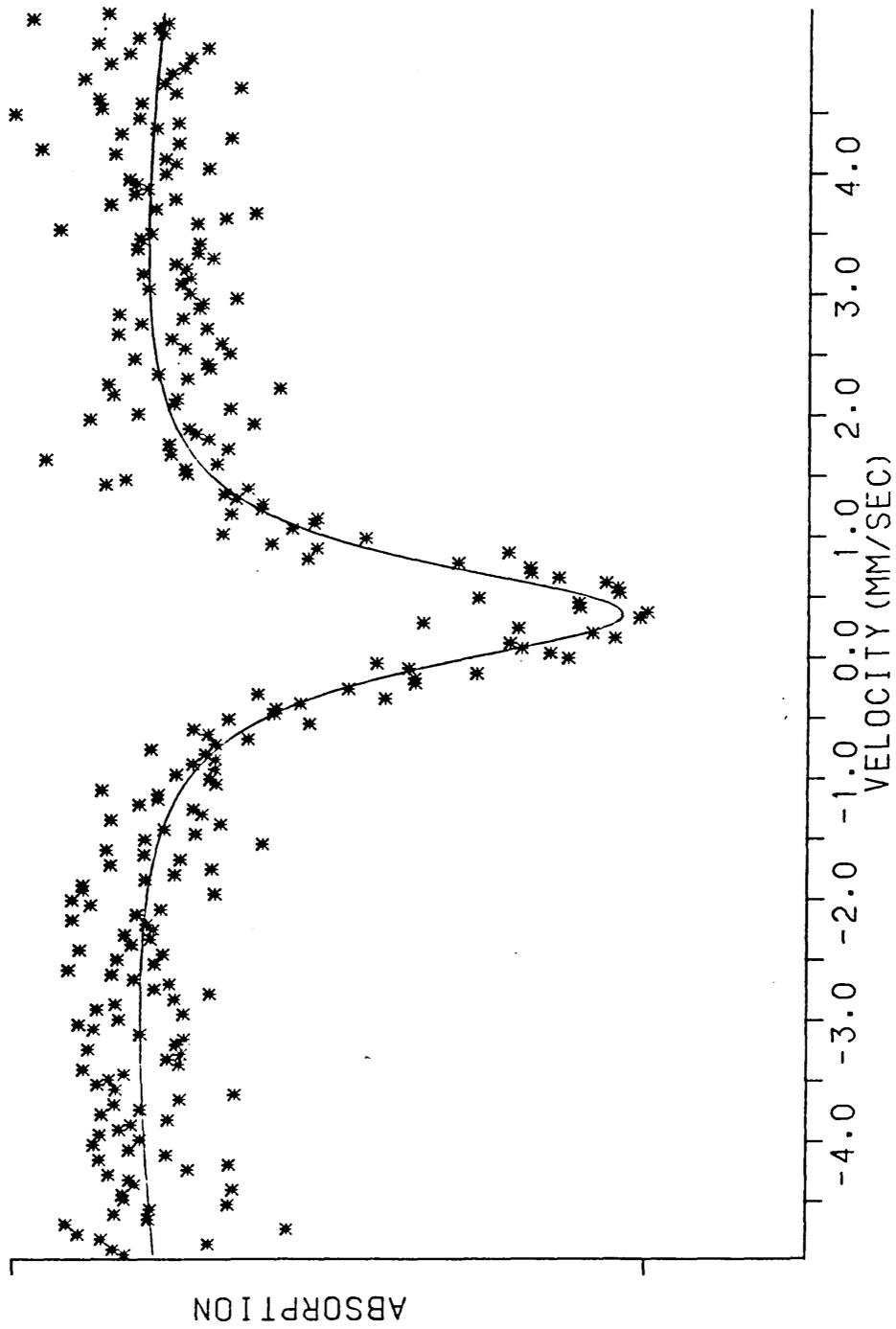
Mössbauer technique to species at low concentration. The Mössbauer lines are Lorentzian in shape and for thin absorbers the line area is proportional to the concentration of the absorbing species if they have similar recoilless fractions. The width of absorption lines, for the compounds studied here, are typically 1 mms^{-1} at half height. Therefore degradation products at low concentration will have broad, low intensity lines and will be very difficult to observe in the spectra considering the long run times and low tin concentrations being studied. The spectra in Figure 3.2 A and B were computer fitted to single Lorentzian lines, which may be an over-simplification, and therefore if low concentrations of other compounds are present the computer fit represents the sum of the Lorentzian lines present. Subsequent irradiation to an exposure of 200 kGy may result in further conversion to the major component of the spectrum and give rise to the observed change in velocity of this line compared with the 100 kGy exposure.

The corresponding solvent cast samples of the thioglycollate stabilisers, [1] and [2], show slightly different behaviour upon irradiation. Figure 3.3A shows the Mössbauer spectrum of dibutyltinbis(isooctylthioglycollate) [2], dispersed in PVC by solvent casting, after an exposure of 100 kGy. From this spectrum, it is clear that the degradation process is not as far advanced as was observed for the milled samples and a multicomponent

Figure 3.3.A ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC (solvent cast) after an Exposure of 100 kGy recorded at 80K
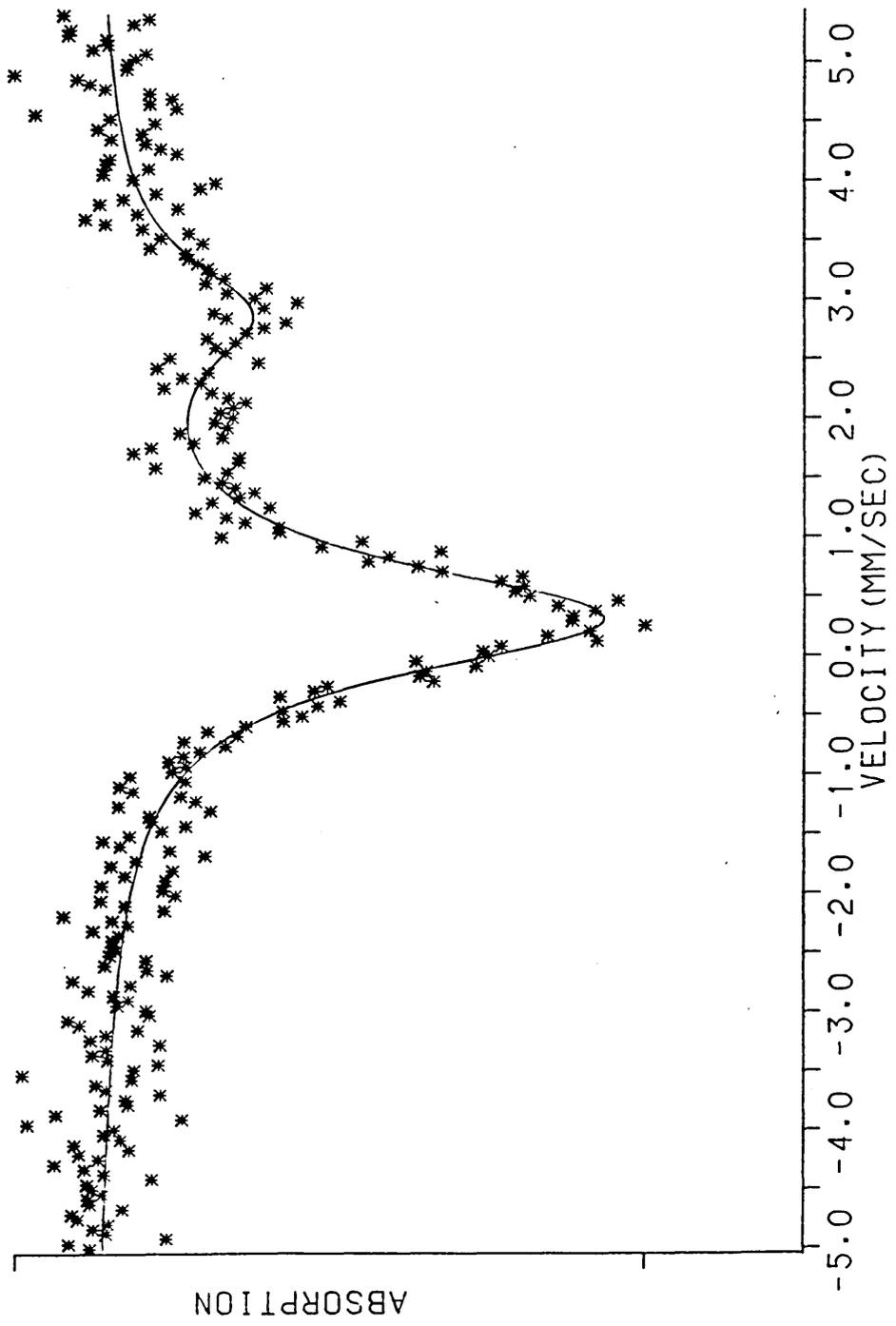
Figure 3.3.B ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in

PVC (solvent cast) after an Exposure of 200 kGy recorded at 80K

- 124 -
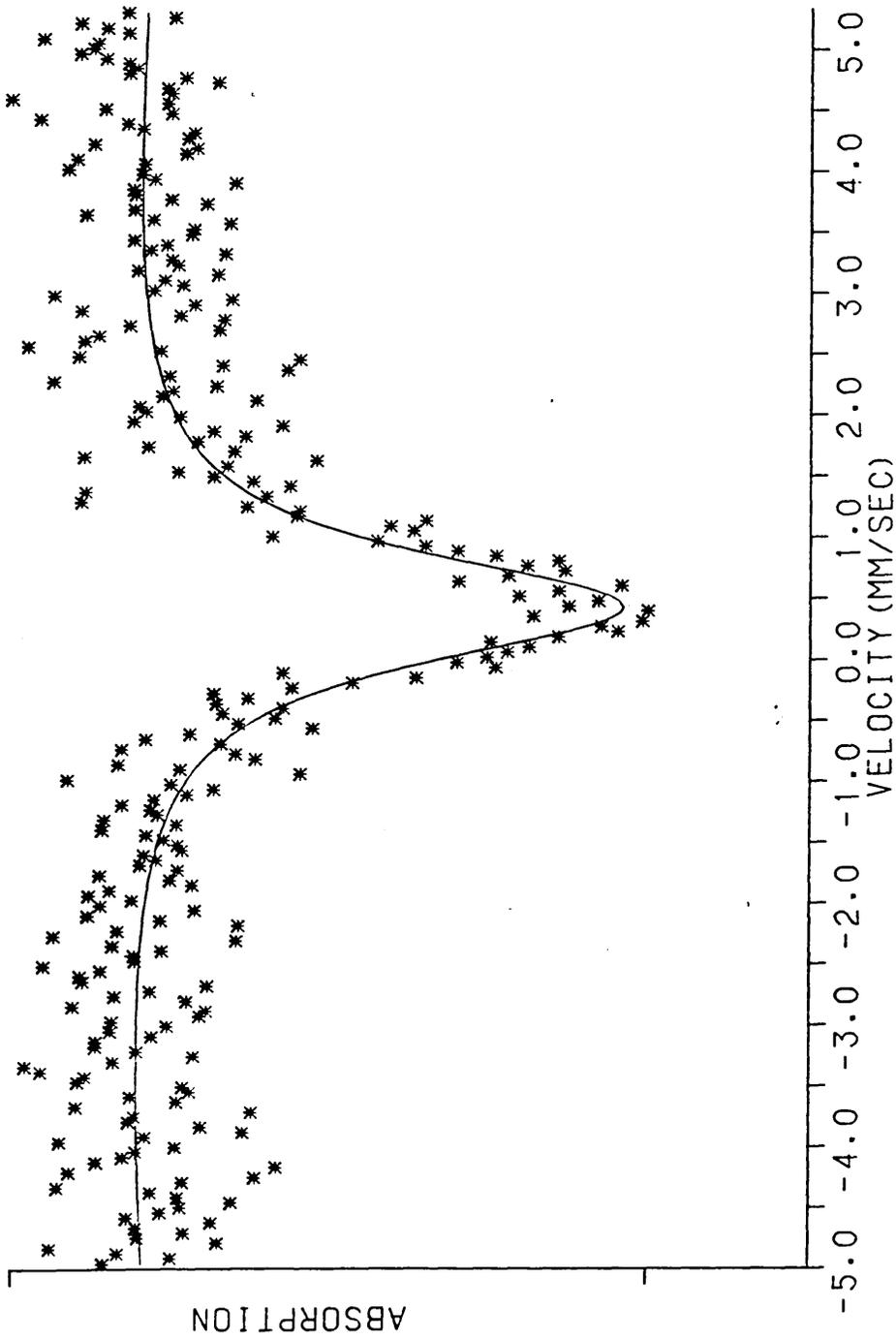
spectrum is observed. It is clear, however, that an analogous degradation process is occurring in the solvent cast sample by the observation that the main component of this spectrum is measured at an isomer shift (δ = 0.36 mms^{-1}) which is close to that observed for the irradiated milled samples containing stabilisers [1] and [2]. In order to obtain further information about the extent of conversion to this component, the spectra for the irradiated solvent cast samples were computer fitted as shown schematically in Figure 3.4. The spectra were computer fitted assuming two components: component A being the single line degradation product, and component B a quadrupole doublet, having both lines with fixed equal width and depth. Component B represented the sum of the unknown number of Lorentzian absorption lines for the degradation products occurring as quadrupole doublets. The isomer shift and quadrupole splitting values obtained for this component therefore could not be used to infer any identification of the species present as it was recognised that this represented a complex super-position of components. However, the ratio of the line areas for the two components could be used to obtain an approximate estimate of the conversion to the single line component which represented the final degradation product. The absorption line areas were obtained by evaluating $A = \Gamma_H$ x Relative depth for each peak.

Figure 3.4 ^{119}Sn Mössbauer Spectrum of Dibutyltinbis-
isooctylthioglycollate) in PVC (solvent cast)
after an Exposure of 100 kGy
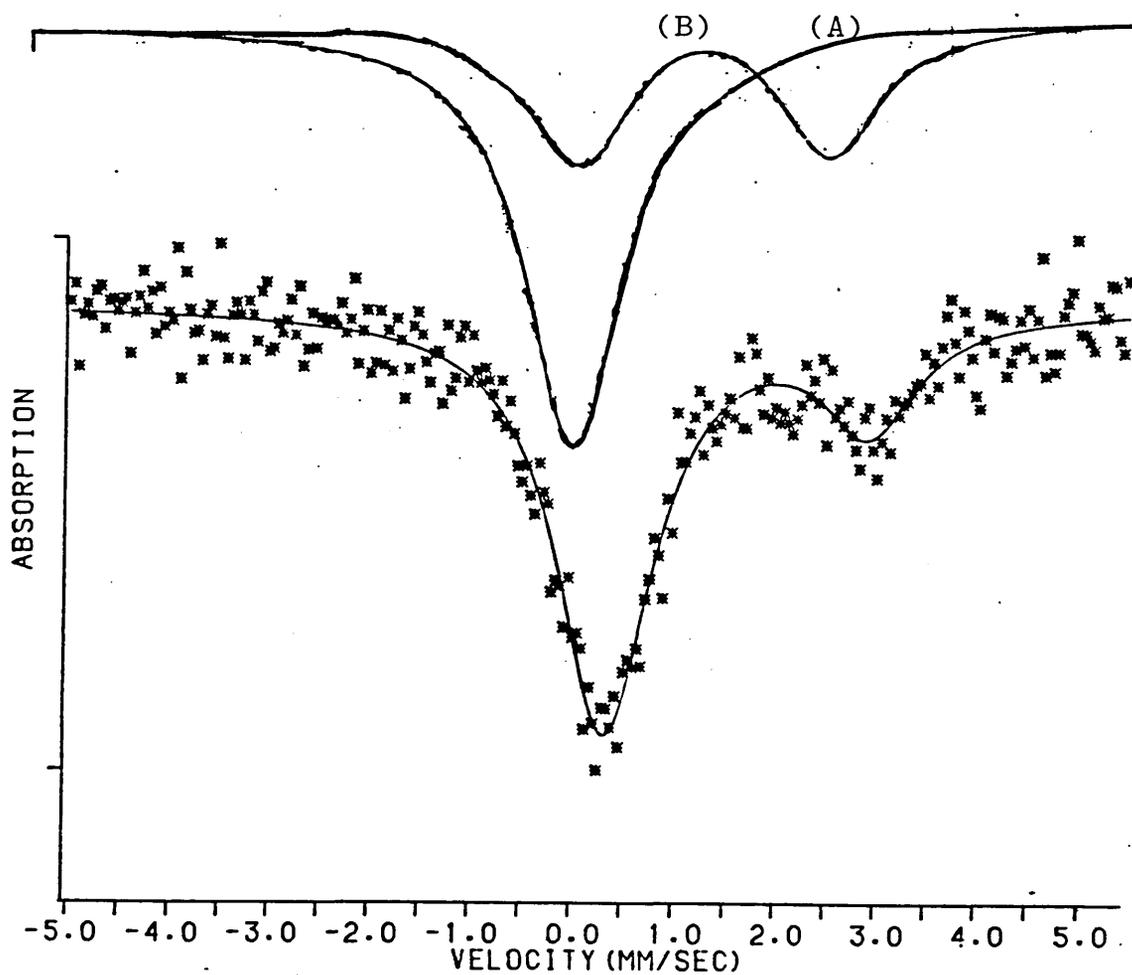
The two components of the computer fit are shown

which correspond to (A) the single 'line' degradation

product and (B) the sum of Lorentzian absorption lines

for degradation products occurring as quadrupole

doublets

The Mössbauer spectra of solvent cast samples of stabilisers [1] and [2] after an exposure of 100 kGy show that the majority of each stabiliser (70%) has been converted to the single line component (δ = 0.36 and 0.34 mms^{-1} respectively). After an exposure of 200 kGy the solvent cast samples show only one major component clearly visible (Figure 3.3B), comparable with the corresponding milled samples. The isomer shifts (δ = 0.32 and 0.34 mms^{-1} respectively) are lower than those observed for the milled samples (δ = 0.40 and 0.41 mms^{-1} respectively) which may indicate that low concentrations of partially degraded stabiliser still remain. The solvent cast samples therefore appear to exhibit a greater stability towards the irradiation process for both the stabiliser and the PVC itself.

For the maleate stabiliser [3] (Table 3.3), after an exposure of 100 kGy, multicomponent spectra have been observed for both milled and solvent cast samples. Figure 3.5A shows the Mossbauer spectrum of milled PVC containing stabiliser [3] after an exposure of 100 kGy, showing partial conversion to the single line degradation product. All the spectra of the maleate stabiliser [3] were computer fitted as a two component system as described earlier. The area ratio of the two components showed, for the milled sample after an exposure of 100 kGy, appreciable conversion (60%) to the single line component (δ = 0.39 mms^{-1}) had occurred. Further conversion (80%) occurs after the 200 kGy exposure

Figure 3.5.A ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylmaleate) in PVC

(milled) after an Exposure of 100 kGy recorded at 80K
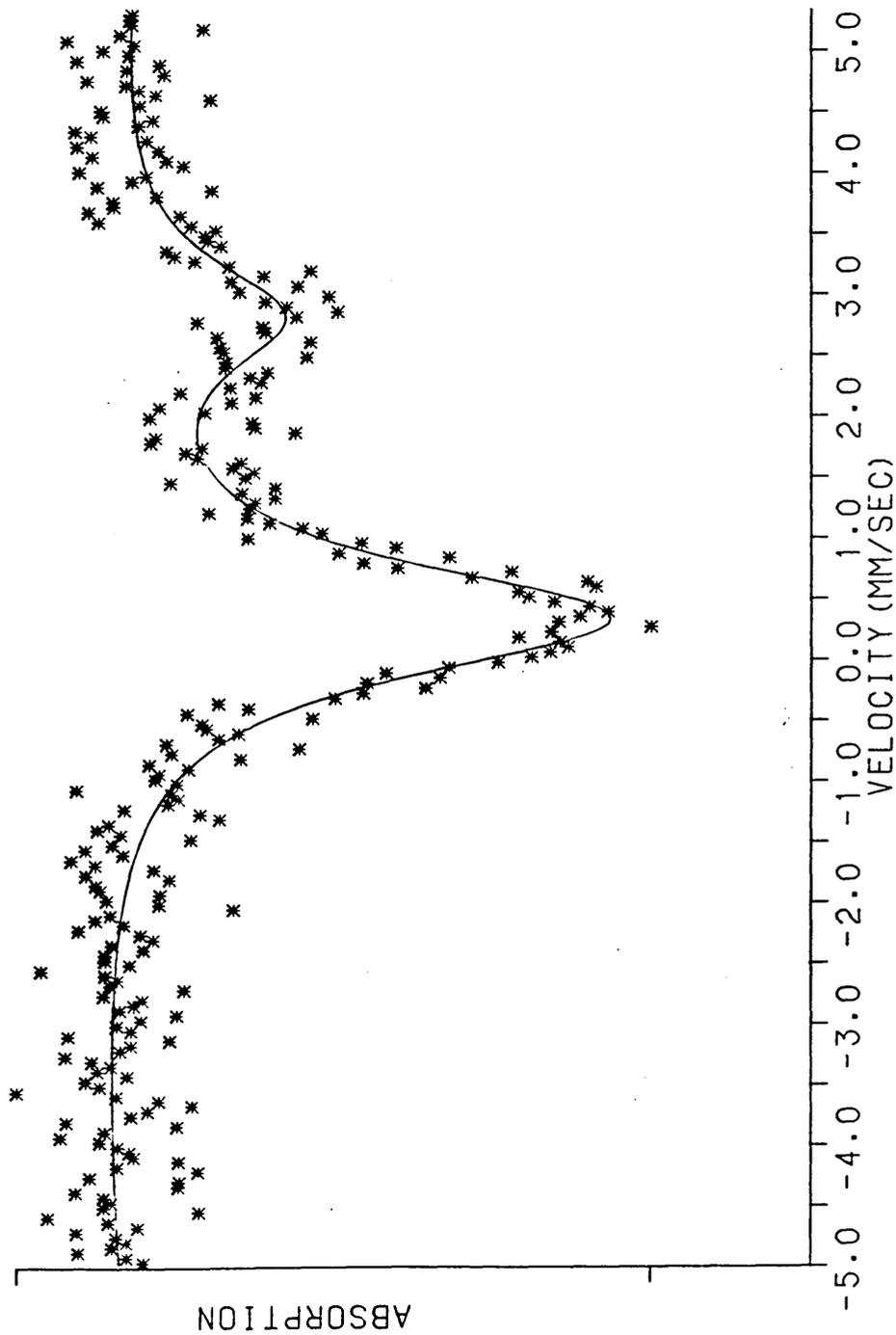
Figure 3.5.B ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylmaleate) in PVC (milled) after an Exposure of 200 kGy recorded at 80K
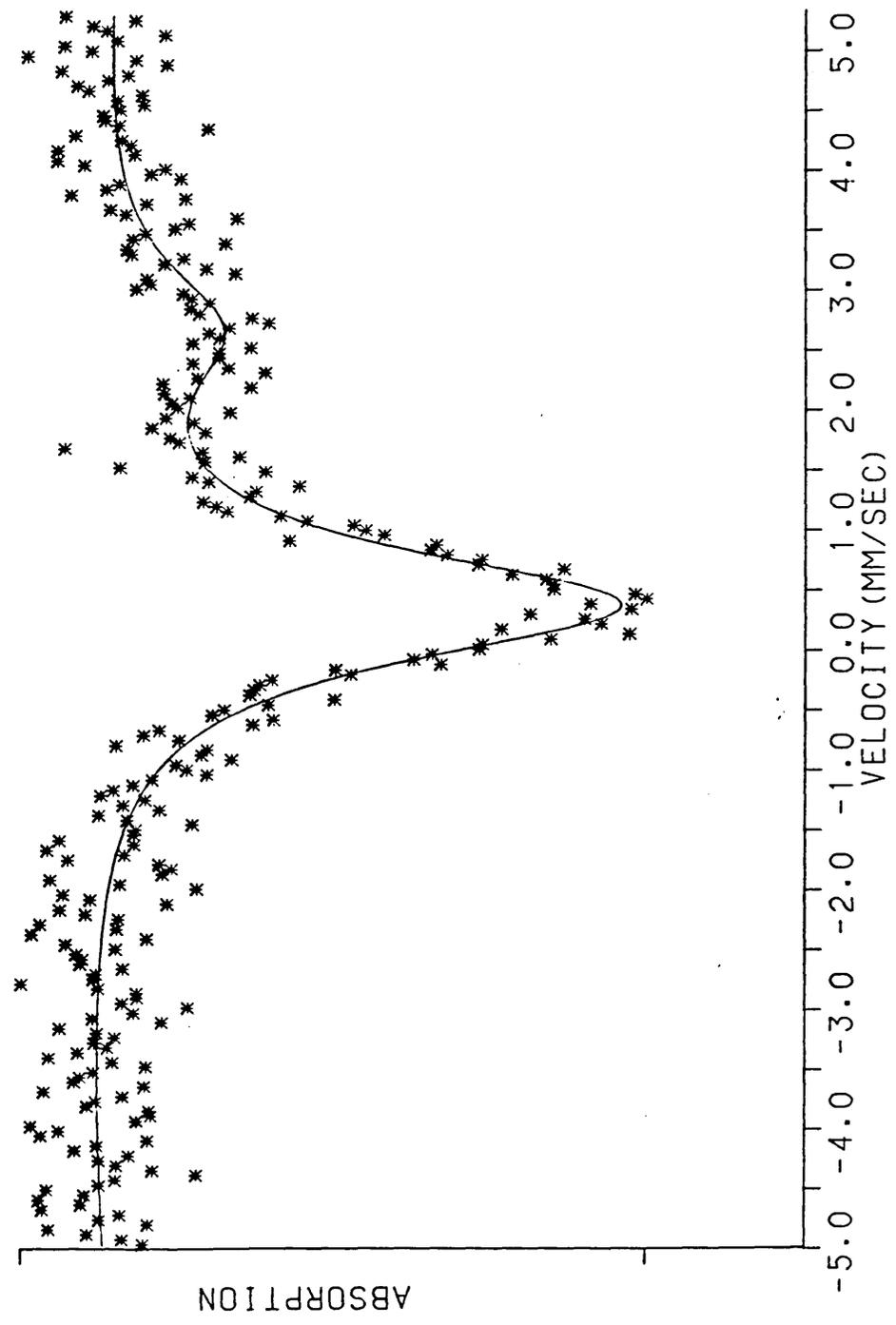
(δ = 0.41 mms^{-1}), as shown in Figure 3.5B. The solvent cast sample has again shown greater resistance to degradation and after 100 kGy much less (20%) conversion to the single line component (δ = 0.37 mms^{-1}) has occurred. After the 200 kGy exposure, further conversion (40%) to this component is observed (δ = 0.40 mms^{-1}).

3.2.1 Identification of the Terminal Degradation Product

In a photochemical degradation study of organotin-stabilised PVC containing dibutyltinbis(isooctylthio-glycollate) [2] using ^{119}Sn Mössbauer spectroscopy, a single line degradation product having parameters similar to those formed in these irradiation studies was reported after prolonged exposure to artificial sunlight.[18] This degradation product was tentatively identified from the observed Mössbauer parameters as stannic oxychloride, $SnOCl_2$, and was suggested to result from the formation of dibutylchlorotin(isooctylthioglycollate) [5] and subsequent elimination-oxidation of the alkyl groups, arising from peroxide oxidation, to yield $SnOCl_2$. This seems an unlikely degradation product in view of the probable reactivity of stannic oxychloride towards hydrogen chloride[19] which will be abundantly present in the degrading PVC. This degradation product may be the same as that observed in the γ-irradiation study.

Stannic chloride, $SnCl_4$, is a likely degradation product which could arise from the dealkylation of any alkyltinchlorides, R_2SnCl_2, which are formed by the

reaction of the stabiliser with hydrogen chloride liberated from the polymer.[13] In studies of the reactions between organotin stabilisers, of the type R_nSnY_{4-n}, and anhydrous hydrogen chloride in a chlorinated hydrocarbon solvent at temperatures used in commercial processing of stabilised PVC (in an evaluation of their potential as thermal stabilisers), cleavage of tin-carbon bonds was observed.[20] The formation of monoalkyltin chlorides or stannic chloride was shown to lead to severe blackening and degradation of the polymer. In other studies,[21] dehydrochlorination of model compounds was shown to be enhanced by an increase in the Lewis acidity of the organotin chloride present. Stannic chloride was shown to be the most effective catalyst for the dehydrochlorination process but the reaction yield was limited and it was suggested that the inhibition of the catalysis is due to the formation of a complex between hydrogen chloride and stannic chloride which competes with the formation of the complex between stannic chloride and the chlorine atoms of the model compound.

However, the isomer shift for pure stannic chloride (δ = 0.82 mms^{-1}), appeared to eliminate it as the degradation product although it gave a single line Mössbauer spectrum. Table 3.5 shows the Mössbauer parameters for stannic chloride in its pure state, when dispersed in PVC (by solvent casting from dichloromethane) and in PVC after an exposure of 200 kGy. After dispersing the stannic chloride in PVC, the polymer became severely

discoloured and turned a dark brown colour which resulted from the catalytic dehydrochlorination of the PVC[21] and formation of polyene sequences in the polymer. The isomer shift for stannic chloride in PVC (δ = 0.30 mms^{-1}) is much lower than that observed for the pure compound (δ = 0.82 mms^{-1}) and is much closer to the isomer shift observed for the degradation product of the stabilisers after irradiation. This may result from the stannic chloride coordinating to the chlorine atoms of the polymer[21] which would result in a decrease in isomer shift for the stannic chloride as a result of a decrease in s-electron density at the tin nucleus[22] (or alternatively due to an increased shielding contribution by p- and d-orbitals). Also a structural change from tetrahedral to octahedral geometry ($SnCl_4$ to $SnCl_6^{2-}$) is known to result in a reduction in the isomer shift (δ = 0.80 to 0.51 mms^{-1} respectively)[22] of such compounds. After an exposure of 200 kGy, the isomer shift for the stannic chloride increases to a value comparable to that observed for the degradation product observed in the milled PVC samples (δ = 0.39 mms^{-1}). This may result from the formation of a stannic chloride-hydrogen chloride complex.[22] Frozen aqueous solutions of the complex ion $[SnCl_6]^{2-}$, resulting from an adduct of stannic chloride and hydrogen chloride, are known to give isomer shifts of this order (δ = 0.45 mms^{-1}),[23] and the observed isomer shift is typical of octahedral stannic chloride complexes in general.[24,25]

Table 3.5 : ^{119}Sn Mössbauer Parameters for Stannic Chloride in PVC (at 1.2% (w/w)) at 80K

Sample	$\delta(mms^{-1})$	$\Delta(mms^{-1})$	$\Gamma(mms^{-1})$
Stannic Chloride Pure	0.82	-	1.32
Stannic Chloride in PVC (solvent cast)	0.30	-	1.24
Stannic Chloride in PVC (solvent cast) after an exposure of 200 kGy	0.39	-	1.06

Parameters ± 0.02 mms^{-1} for pure materials and

± 0.05 mms^{-1} when dispersed in PVC

From the above results, it seems that a number of interactions are possible when stannic chloride is dispersed in PVC, which may account for the observed broad line width (Γ = 1.24 mms^{-1}) upon initial dispersion in the polymer. The terminal degradation product seems likely to be stannic chloride which is stable upon an exposure of 200 kGy when dispersed in the PVC.

3.3 CONCLUSIONS

In general the parameters for the organotin stabilisers [1], [2] and [3] when dispersed in PVC by milling and solvent casting show that the stabilisers can be satisfactorily dispersed in PVC without significant degradation occurring, and therefore the degradation products after irradiation can be principally assigned to the irradiation process.

The preliminary irradiation studies show that the terminal degradation product, under the conditions used, for both the thioglycollate and maleate stabilisers is stannic chloride, which is associated with the polymer or polymer degradation products. Both stannic chloride and the degradation product observed for the organotin stabilisers undergo no further transformation after an exposure of 200 kGy in PVC.

These results show that the degradation process has extended beyond that observed in the thermal degradation of similar systems.[13,26] The terminal degradation

product seems likely to be stannic chloride, resulting from the following degradation process:

(i) $R_2SnY_2 \xrightarrow{PVC.\gamma} R_2SnYCl + HY$ (1)

(ii) $R_2SnYCl \xrightarrow{PVC.\gamma} R_2SnCl_2 + HY$ (2)

(iii) $R_2SnCl_2 \xrightarrow{PVC.\gamma} RSnCl_3 + HR$ (3)

(iv) $RSnCl_3 \xrightarrow{PVC.\gamma} SnCl_4 + HR$ (4)
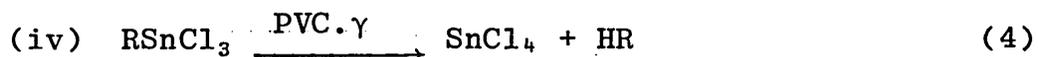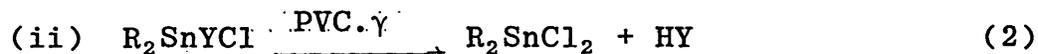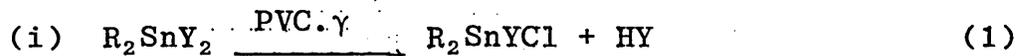
(R = Oct or Bu, Y = maleate or thioglycollate)

The final state of the stannic chloride in reaction (4) is likely to be as a six-coordinate complex with hydrogen chloride, $[H_2SnCl_6]$, which is liberated from the polymer.

The milled PVC samples containing stabilisers [1], [2] and [3] undergo greater conversion to stannic chloride after an exposure of 100 kGy and the polymer is discoloured to a greater extent compared with the corresponding solvent cast samples. This may reflect the sample preparation, since radicals and peroxides produced during the milling process could sensitise the polymer to degradation in the γ-irradiation process.

The degradation product observed by Brooks et al[18] in a [119m]Sn Mössbauer study of photochemically degraded PVC containing dibutyltinbis(isooctylthioglycollate) [2]

seems likely to be stannic chloride and not stannic oxychloride as reported. This indicates that analogous processes may occur during ultraviolet-and γ-irradiation of organotin-stabilised PVC. Brooks et al also showed that, after prolonged uv-irradiation of PVC containing dibutyltinbis(isooctylmaleate) [3], the stabiliser underwent no observable degradation, appearing to remain intact. However, as has been demonstrated in this study, the high energy γ-photons (1.33 MeV) from the ^{60}Co source, have induced Sn-O and Sn-C bond cleavage in this compound. Much less conversion to stannic chloride is observed for the maleate stabiliser [3] than for the thioglycollate stabilisers [1] and [2]. This may merely reflect its higher concentration (2% (w/w)) compared to the thio-glycollate stabilisers (1.2% (w/w)), producing a corresponding increase in stabilisation. Alternatively, the increased stability may reflect an inherent stability, as observed in ultraviolet degradation studies[18] with this stabiliser, to high energy photons.

3.4 REFERENCES

1. K. Figge and W. Freytag, <u>Dtsch. Lebens R</u>, 1977, <u>7</u>, 205.

2. M. Foure and P.E. Rakita, <u>Med. Device and Diag. Ind.</u>, 1983, <u>5</u>, 33.

3. E.S. Josephson, <u>J. Food Safety</u>, 1983, <u>5</u>, 161.

4. W.S. Penn, <u>'PVC Technology'</u>, Eds. W.V. Titow and B.J. Lanham, 3rd edn., Applied Science, London, 1971.

5. B.B. Cooray and G. Scott, <u>In Developments in Polymer Stabilisation - 2</u>, Ed. G. Scott, Applied Science, London, 1980, p 54.

6. M. Pike and W.F. Watson, <u>J. Polym. Sci.</u>, 1952, <u>9</u>, 229.

7. D.J. Angier and W.F. Watson, <u>J. Polym. Sci.</u>, 1955, <u>18</u>, 129; 1956, <u>20</u>, 235.

8. G. Ayrey, C.G. Moore and W.F. Watson, <u>J. Polym. Sci.</u>, 1956, <u>19</u>, 1.

9. S.E. Bresler, S.N. Zhurkov, E.N. Kazbekov, E.M. Saminskuv, and E.E. Tomaskevskii, <u>Zhur. Tekh. Fiz.</u>, 1959, <u>29</u>, 358.

10. G. Scott, M. Tahan and J. Vyvoda, <u>Europ. Polym. J.</u>, 1978, <u>14</u>, 913.

11. G. Scott, M. Tahan and J. Vyvoda, <u>Europ. Polym. J.</u>, 1979, <u>15</u>, 51.

12. P.G. Harrison, T.J. King and M.A. Healy,
    J. Organometal. Chem., 1979, 182, 17.

13. A. Frye, R.W. Horst and M.A. Paliobagis,
    J. Polym. Sci., A, 1964, 2, 1765.

14. P.B. Simons and W.A.G. Graham, J. Organometal. Chem.,
    1967, 8, 479.

15. G.M. Bancroft and T.K. Sham, Can. J. Chem., 1972,
    54, 1361.

16. B.W. Fitzsimmons, N.J. Seeley and A.W. Smith,
    J. Chem. Soc., (A), 1969, 143.

17. W.D. Honnick and J.J. Zuckerman, J. Organometal. Chem.,
    1979, 178, 133.

18. J.S. Brooks, R.W. Clarkson, D.W. Allen, M.T.J. Mellor
    and A.G. Williamson, Polym. Deg. and Stab., 1982,
    4, 359.

19. I.R. Beattie and V. Fawcett, J. Chem. Soc. (A), 1967,
    1583.

20. B.W. Rocket, M. Hadlington and W.R. Poyner,
    J. Appl. Polym. Sci., 1974, 18, 745.

21. T. Van Hoang, A. Michel and A. Guyot, Polym. Deg.
    and Stab., 1982, 4, 213.

22. R.V. Parish, In Progress in Inorganic Chemistry, Ed.,
    S.J. Lippard, Wiley Interscience Publishers, 1972,
    15, 132.

23. M. Katada, H. Kanno and H. Sano, _Polyhedron_,
     1983, _2_, 104.

24. D. Tudela, V. Fernandez and J.D. Tornero, _J. Chem._
     Soc., Dalton Trans., 1985, 1281.

25. S.J. Blunden, D. Searle and P.J. Smith, _Inorg. Chim._
     Acta, 1985, _98_, 185.

26. D.W. Allen, J.S. Brooks, R.W. Clarkson, M.T.J. Mellor,
     and A.G. Williamson, _J. Organometal. Chem._, 1980,
     _199_, 299.

CHAPTER 4 : VARIABLE DOSE IRRADIATION STUDY OF POLY(VINYLCHLORIDE) CONTAINING DIBUTYLTINBIS(ISOOCTYLTHIOGLYCOLLATE)

4.1   INTRODUCTION

4.2   RESULTS AND DISCUSSION

4.2.1 INFRARED STUDIES OF IRRADIATED POLY(VINYLCHLORIDE) FILMS CONTAINING DIBUTYLTINBIS(ISOOCTYLTHIO-GLYCOLLATE)

4.2.2 MODEL IRRADIATION STUDIES OF POLY(VINYLCHLORIDE) CONTAINING DEGRADATION INTERMEDIATES

4.3   CONCLUSIONS

4.4   REFERENCES

4.1 INTRODUCTION

The work discussed in Chapter 3 on the initial irradiation studies of PVC containing the stabilisers dioctyltinbis(isooctylthioglycollate) [1], dibutyltinbis(isooctylthioglycollate) [2] and dibutyltinbis(isooctylmaleate) [3] indicates that extensive degradation of both the polymer and stabiliser has occurred after an exposure of 100 kGy. The degradation process of the stabiliser has extended beyond that in thermal and photochemical degradation of these systems since degradation products such as the alkylchlorotin thioglycollate [4], [5] and maleate [6] or dialkyltin dichloride were not identified as the major degradation products at the exposures studied.

For the thioglycollate stabilisers [1] and [2] in milled PVC, conversion to stannic chloride appears to be complete and, at the exposures studied, little information can be gained about the degradation products which precede this terminal product. However, their presence can be seen in the irradiated solvent cast samples containing [1] and [2] and those containing [3] after the 100 kGy exposure. Food irradiation legislation in this country only allows food to be exposed to a maximum dose of 10 kGy,[1] and therefore degradation products at exposures up to 10 kGy need to be identified. The degradation products identified at lower exposures will help to substantiate the proposed degradation pathway of the stabilisers suggested in Chapter 3.

The PVC used as food packaging material will have been
subjected to thermal forming of some kind and will
already contain a mixture of degradation products as
observed by the Mössbauer parameters of milled PVC in
Chapter 3. Therefore milled PVC containing
dibutyltinbis(isooctylthioglycollate) [2]   (1.2% (w/w))
was used in the investigation of exposures of
irradiation from 1 to 100 kGy in order to simulate such
sample characteristics. The Mössbauer spectrum was
recorded for each PVC sample after progressive exposure
to γ-irradiation.

4.2   RESULTS AND DISCUSSION

The progressive degradation of PVC containing
dibutyltinbis(isooctylthioglycollate) [2] upon
increasing radiation exposure can be observed by the
increasing discolouration of the clear polymer samples.
A gradual yellowing of the polymer occurs which
eventually results in a black discolouration after a 50 kGy
exposure. Figure 4.1 shows a plot of optical density of
the PVC samples as a function of exposure. The plot
shows that exposures up to 20 kGy show a steady increase
in the degradation of the PVC, due to the build-up of
polyene sequences. At higher exposures a rapid darkening
of the PVC is initiated until the polymer is opaque after
an exposure of 50 kGy.

Figure 4.1 Discolouration of Milled PVC containing
Dibutyltinbis(isooctylthioglycollate) as a
Function of Irradiation Exposure
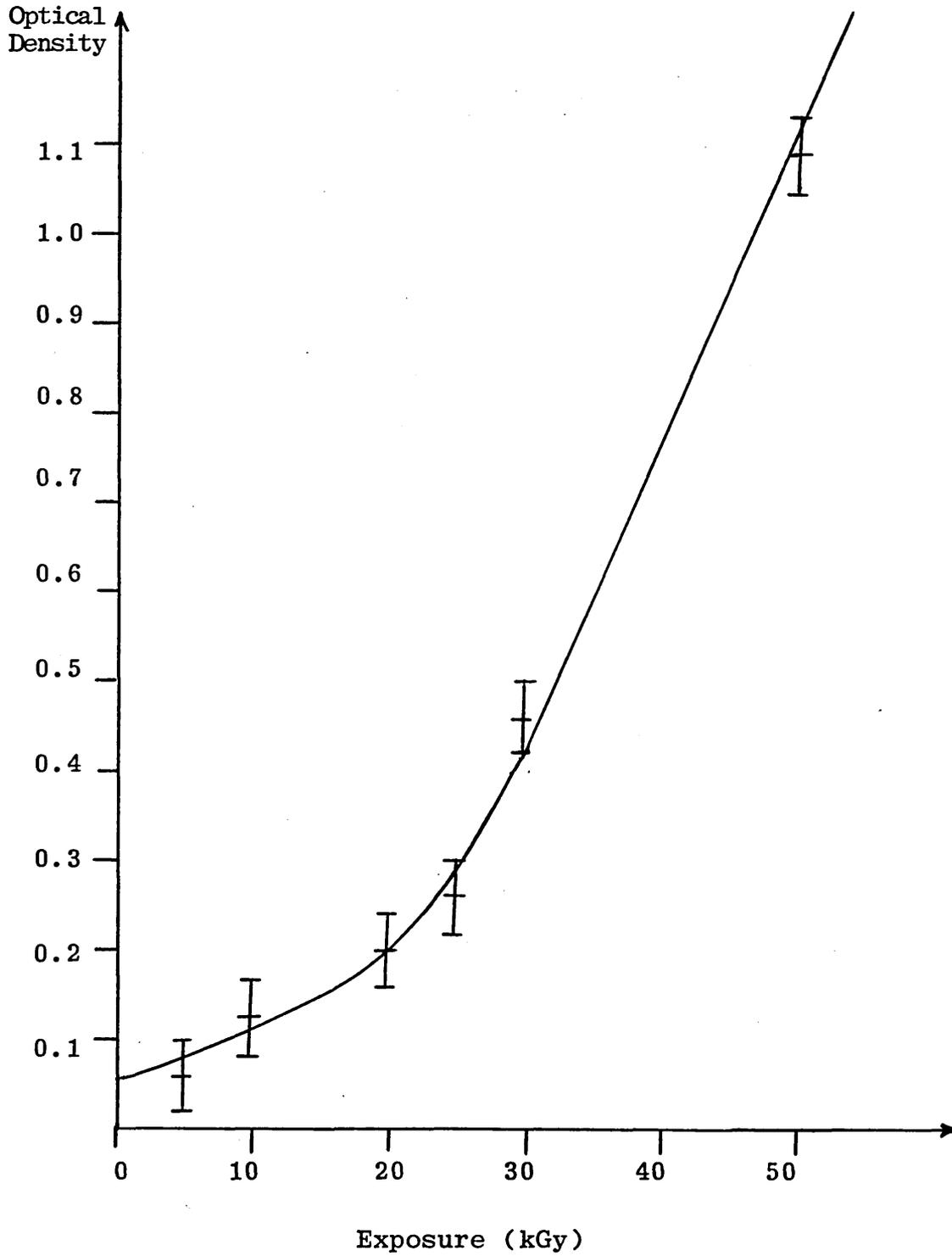
The Mössbauer spectra of the progressively exposed
milled PVC samples containing dibutyltinbis(isooctyl-
thioglycollate) [2] are shown in Figure 4.2A-K. The
spectra show the gradual conversion of the stabiliser
to stannic chloride over the exposure range and, after
100 kGy, only one component is clearly seen. At
intermediate exposures, complex spectra are observed
which contain overlapping lines which correspond to the
undegraded stabiliser and degradation products. An
attempt was made to computer fit the data in these
spectra to Lorentzian lines with parameters corresponding
to those observed for the proposed degradation inter-
mediates when dispersed in PVC. The spectra were complex
and could not be fitted as simple mixtures of these
components.

The line positions for the stabiliser [2] and subsequent
degradation products when individually dispersed in PVC
are given in Table 4.1 This data shows that all the
possible components of the spectra observed in Figure 4.2
have an absorption line close to zero velocity. Similarly
the high velocity lines of the quadrupole doublets for di-
butylchlorotin thioglycollate [5] and dibutyltin
dichloride will overlap significantly. After irradiation,
if a number of these degradation products arise together,
then considerable overlap of the absorption lines will
occur. Figure 4.3 shows the Mössbauer spectrum of
dibutyltinbis(isooctylthioglycollate) [2] with the line
positions for the four degradation products, when dispersed
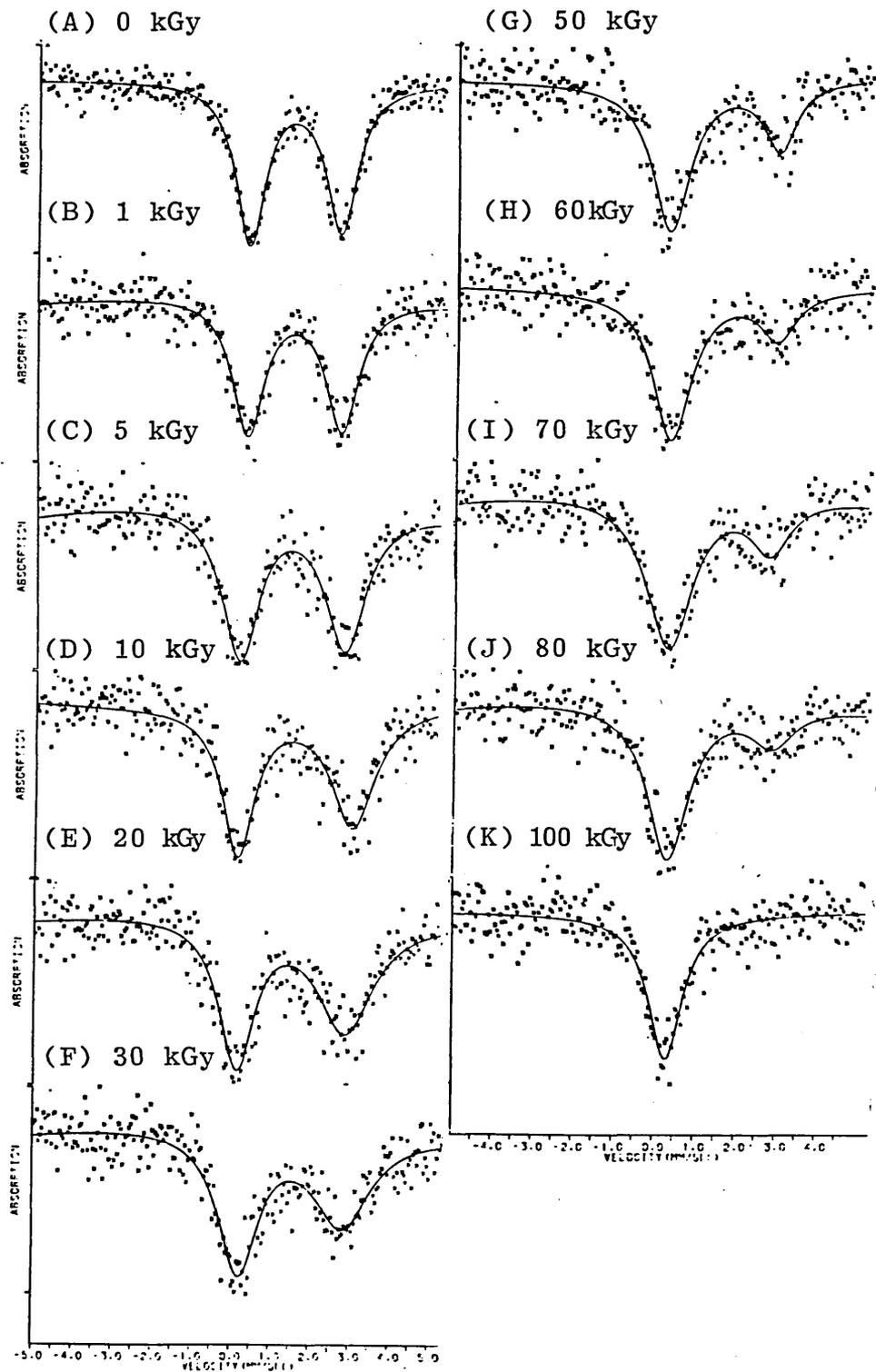
Figure 4.2.A-K ^{119}Sn Mössbauer Spectra of Samples of Dibutyltinbis(isooctylthioglycollate) in PVC (milled) after Exposures of Irradiation between 0 and 100 kGy recorded at 80K

Table 4.1 : ^{119}Sn Mössbauer Absorption Line Positions for Dibutyltinbis(isooctylthioglycollate) and Subsequent Degradation Products when Dispersed in PVC (1.2% (w/w)) at 80K

Sample	Line Position (mms^{-1})	
	Line 1	Line 2
Bu$_2$Sn(IOTG)$_2$ (milled)	0.31	2.62
Bu$_2$SnCl(IOTG)$_2$ (milled)	-0.06	2.93
Bu$_2$SnCl$_2$ (solvent cast)	-0.02	3.01
BuSnCl$_3$ (solvent cast)	0.20	2.14
SnCl$_4$ (solvent cast)	0.30	-

Parameters ± 0.05 mms^{-1}

Figure 4.3 ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC (milled) with the likely Absorption Line Positions of the Possible Degradation Products (A) Dibutylchlorotin thioglycollate, (B) Dibutyltin Dichloride, (C) Dibutyltin trichloride and (D) Stannic Chloride
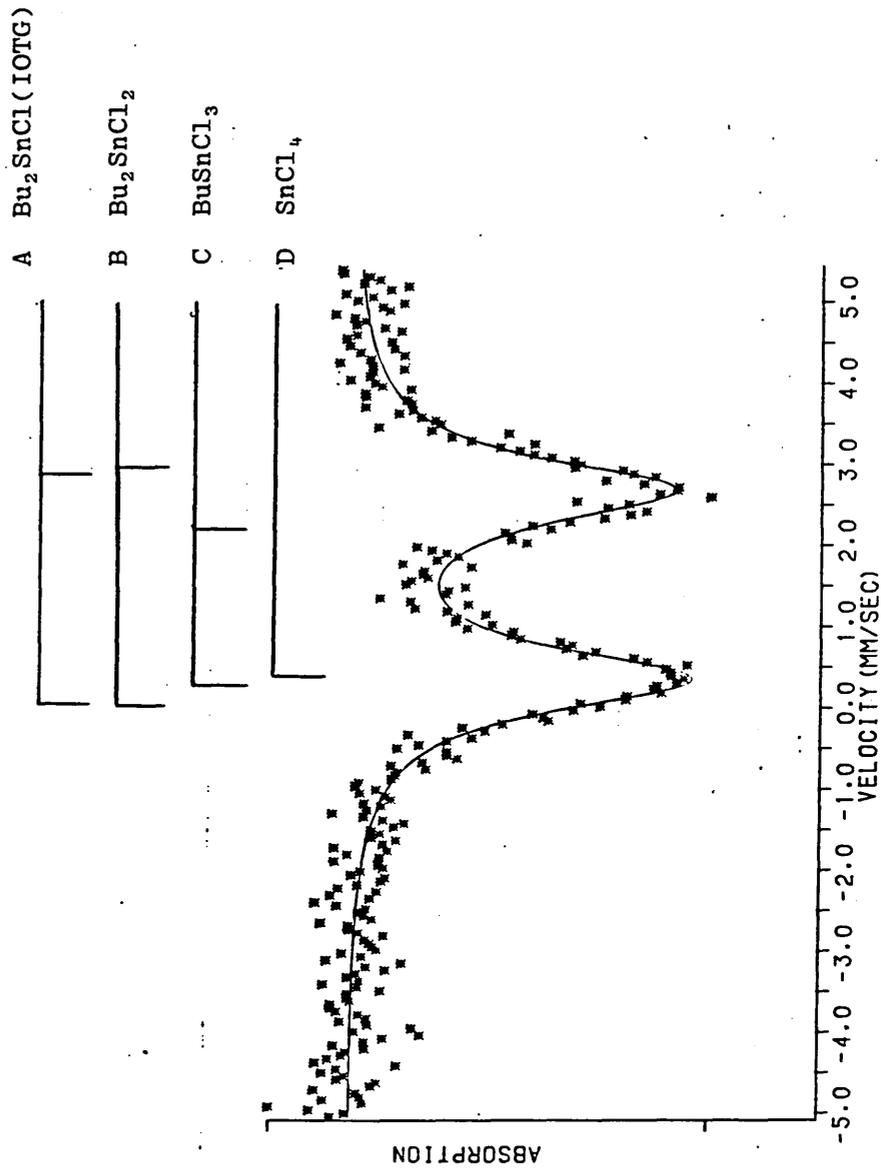
in PVC, also indicated on the spectrum. From this, the severe convolution of the broad ($\Gamma \sim 1.00$ mms^{-1}) absorption lines can be observed. Therefore, if mixtures of these degradation products arise in the irradiated PVC, at unknown concentrations, it will be very difficult to computer fit the data for the unresolved lines. Those components at low concentration will have a correspondingly low absorption line area which will result in low intensity Lorentzian lines. These lines, which may be broad, would overlap to a large extent with those of other components of the spectra which will make their resolution very difficult.

The spectra in Figure 4.2 were found to be of this complex nature and could not be successfully computer fitted as a number of Lorentzian lines corresponding to the individual degradation products. The solid line in these spectra represents the sum of the Lorentzian lines of these components. Each spectrum was computer fitted as though it consisted of only 2 Lorentzian lines, which represent the sum of the components present. Each line was computer fitted to obtain its position, width and depth. These two 'lines' in the spectra of irradiated PVC samples will therefore appear broadened ($\Gamma > 1.00$ mms^{-1}) because mixtures of components are present with slightly different line positions. The spectra computer fitted by this method have been analysed in terms of the individual 'line' parameters as shown in Table 4.2. Several interesting points are revealed by the data which substantiate the proposed degradation pathway for dibutyltinbis(isooctylthioglycollate) [2].

Table 4.2 : The Mössbauer Line Positions Observed after Irradiation of Dibutyltinbis(isooctyl-thioglycollate) in PVC (milled) after Exposures between 0 and 100 kGy

| Exposure (kGy) | Line 1 | | | | Line 2 | | | | $\dfrac{\text{Area Line 1}}{\text{Area Lines 1 + 2}}$ |
	Position (mms^{-1})	Width (mms^{-1})	Relative Intensity	Relative Area	Position (mms^{-1})	Width (mms^{-1})	Relative Intensity	Relative Area	
0	0.31	0.95	1.00	0.96	2.62	0.95	1.00	0.96	0.50 (5)
1	0.27	1.00	1.00	1.00	2.68	1.02	0.96	0.98	0.51 (5)
5	0.07	1.16	1.00	1.16	2.71	1.26	0.92	1.16	0.50 (5)
10	0.04	1.00	1.00	0.99	2.93	1.34	0.82	1.10	0.47 (5)
20	0.07	1.12	1.00	1.12	2.81	1.74	0.78	1.34	0.46 (5)
30	0.17	1.26	1.00	1.26	2.81	1.78	0.67	1.19	0.51 (5)
50	0.24	1.14	1.00	1.14	2.97	0.96	0.45	0.43	0.73 (5)
60	0.28	1.22	1.00	1.22	2.88	1.58	0.31	0.49	0.81 (5)
70	0.28	1.40	1.00	1.42	2.81	1.16	0.34	0.39	0.78 (5)
80	0.29	1.28	1.00	1.28	2.92	1.28	0.24	0.31	0.81 (5)
100	0.34	1.02	1.00	1.02					1.00 (5)

(Parameters ± 0.05 mms^{-1})

After an exposure of only 1 kGy, initiation of the
degradation of the PVC and stabiliser is indicated by
the change in line positions for the quadrupole doublet.
As the exposure is increased to 20 kGy, the position
of the lower velocity 'line', line 1, gradually shifts
to lower velocity (0.07 mms^{-1}) from the original line
position of the stabiliser (0.31 mms^{-1}). The high
velocity 'line', line 2, of the quadrupole doublet
gradually moves to higher velocity (2.81 mms^{-1}) from
its original position (2.62 mms^{-1}) indicating significant
contribution of either dibutylchlorotin thioglycollate
[5] or dibutyltin dichloride or a mixture of these to
the spectrum. Line 2 is very broad (1.74 mms^{-1}) after
this exposure showing the presence of not only these
components but others, which may result from the
undegraded stabiliser [2] or butyltin trichloride. After
the 10 kGy exposure, the intensity of line 2 decreases
steadily upon increasing exposure with respect to line 1.
This should be expected for the suggested degradation
products since their quadrupole doublets would produce
an intense absorption region where the low velocity lines
overlap in line 1. Also the formation of stannic chloride,
a singlet, will contribute only to the absorption in
this line. Conversely, a decrease in intensity of line 2
would be expected since the higher velocity lines of the
quadrupole doublets are spread over a larger velocity
range (Table 4.1), thus resulting in the broader low
intensity line observed. Upon increasing exposure,

conversion of the intermediate degradation products to stannic chloride is observed since the position of line 1 increases gradually towards that of stannic chloride as its contribution becomes more dominant. The absorption area of line 2 will therefore decrease correspondingly as the degradation products are converted to the single line component. After the 100 kGy exposure, any contribution from line 2 is difficult to observe and the line width (Γ = 1.02 mms^{-1}) indicated that only one major component remained. The spectrum after this exposure was fitted as a single Lorentzian line. This may be an over-simplification since the Mössbauer technique is insensitive to contributions by components at low concentration.

The absorption line areas of lines 1 and 2 are proportional to the concentration of the components present in the spectrum. Therefore, since the degradation products, dibutylchlorotin thioglycollate [5], dibutyltin dichloride and butyltin trichloride (and the stabiliser [2]) give rise to quadrupole doublets, having an equal contribution in area to each of lines 1 and 2 when present, then the difference in area of these lines at any exposure can be attributed to stannic chloride which is a single line. Figure 4.4 shows the plot of the absorption area of line 1 as a function of the total absorption area versus exposure. The slope of the line shows that up to an exposure of 20 kGy, the areas of lines 1 and 2 are relatively equal, showing that no

Figure 4.4   Dependence of the Area Ratios of the Absorption
Lines for Degraded Dibutyltinbis(isooctylthioglycollate)
in milled PVC as a function of Exposure Dose

appreciable formation of stannic chloride has occurred. After further exposure, the slope of the line increases sharply and stays relatively constant. This increase in the slope corresponds to the formation of stannic chloride at the low velocity position. This sharp increase in slope after the 20 kGy exposure also corresponds with the onset of rapid discolouration of the PVC (Figure 4.1). Stannic chloride is known to catalyse the dehydrochlorination of PVC, and after its formation as a degradation product cause rapid blackening of the polymer,[2,3] which is observed from Figure 4.1.

4.2.1 Infrared Studies of Irradiated Poly(vinylchloride) Films containing Dibutyltinbis(isooctylthioglycollate)

The Mössbauer data for the pure thioglycollate stabilisers [1] and [2] (ΔE_Q = 2.34 mms^{-1} and 2.29 mms^{-1} respectively) are indicative of four-coordinate structures:

R = Oct [1]
R = Bu   [2]

$$R\diagdown \atop R\diagup Sn \diagup^{S-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_8H_{17}}_{S-CH_2 \underset{\underset{\displaystyle O}{\|}}{C}-OC_8H_{17}}$$

($\nu_{C=O}$ = 1730 cm^{-1})

Infrared data also supports this suggestion since the carbonyl stretching frequency at 1730 cm^{-1} is typical of

an uncoordinated carbonyl group. The higher quadrupole splitting (ΔE_Q = 2.96 mms^{-1} and 2.88 mms^{-1} respectively) for the dialkylchlorotin thioglycollates [4] and [5] is typical of five-coordinate tin with a trigonal bipyramidal structure:
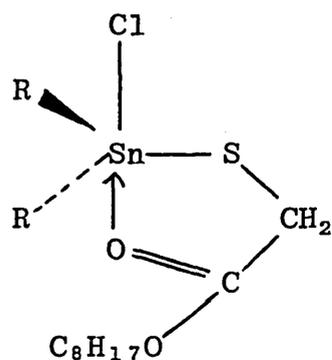
R = Oct [4]

Bu [5]

($\nu_{C=O}$ = 1670 cm^{-1})

It has been demonstrated by several workers,[4,5] that after thermal degradation of PVC containing dibutyltinbis-(isooctylthioglycollate) [2], conversion of the stabiliser to the dibutylchlorotin thioglycollate [5] can be observed in the infrared spectrum of the PVC films. Infrared spectra were recorded for PVC films (prepared by solvent casting from dichloromethane) containing [2] and [5] and for γ-irradiated PVC films containing the stabiliser [2]. The carbonyl stretching frequencies for the pure stabiliser [2] ($\nu_{C=O}$ = 1730 cm^{-1}) and the dibutylchlorotin thioglycollate [5] ($\nu_{C=O}$ = 1670 cm^{-1}) were unchanged when dispersed in PVC.

After an exposure of 10 kGy, PVC film containing the

stabiliser [2] showed the appearance of a further carbonyl stretching frequency ($\nu_{C=O} = 1670$ cm^{-1}), showing conversion of the stabiliser [2] to the dibutylchlorotin thioglycollate [5]. Further exposures up to 50 kGy of similar PVC films showed an increase in intensity of this band as a result of further conversion to [5]. After an exposure of 100 kGy, a low intensity band was still present at 1670 cm^{-1} but after an exposure of 200 kGy this band was absent which indicated conversion of [5] to other degradation products. This suggests that the initial result of the irradiation process is the dehydrochlorination of the polymer. The hydrogen chloride produced reacts with the stabiliser to form the dibutylchlorotin thioglycollate [5].

4.2.2 Model Irradiation Studies of Poly(vinylchloride) containing Degradation Intermediates

To substantiate the proposed degradation scheme for dibutyltinbis(isooctylthioglycollate) [2], ie:

(i) $Bu_2Sn(IOTG)_2 \xrightarrow[\rightarrow]{PVC \ \gamma} Bu_2SnCl(IOTG) + H(IOTG)$

(ii) $Bu_2SnCl(IOTG) \xrightarrow[\rightarrow]{PVC \ \gamma} Bu_2SnCl_2 + H(IOTG)$

(iii) $Bu_2SnCl_2 \xrightarrow[\rightarrow]{PVC \ \gamma} BuSnCl_3 + BuH$

(iv) $BuSnCl_3 \xrightarrow[\rightarrow]{PVC \ \gamma} SnCl_4 + BuH$

each of the products in reactions (i) - (iv) were dispersed in PVC separately (at 1.2% (w/w)) and given an exposure of 200 kGy. Each of the degradation products

should be converted to stannic chloride after this exposure indicating that these are the degradation products which occur throughout the exposure range studied.

The Mössbauer parameters for the stabiliser [2] and the degradation intermediates in their pure states and when dispersed in PVC, given in Table 4.3, are all quadrupole doublets with large splittings, except for the terminal degradation product, stannic chloride. After the 200 kGy exposure, each is converted to stannic chloride (Table 4.4). The spread of isomer shift values observed in Table 4.4 is probably due to an over-simplification of the fitting procedure for these spectra, which were fitted to single Lorentzian lines, when it is likely that small concentrations of the intermediate degradation products still remain in some of the samples. These results indicate that the proposed degradation scheme (i) - (iv) does occur. Upon irradiation, the stabiliser [2] reacts with the hydrogen chloride liberated from the polymer to form initially the dibutylchlorotin thioglycollate [5], as seen from the infrared studies (Section 4.2.1), and then dibutyltin dichloride. At the high absorbed energies resulting from the irradiation process the de-alkylation of dibutyltin dichloride occurs. Since chlorine radicals will be predominant in the PVC as a result of the cleavage of C-Cl bonds, the formation of stannic chloride is the most likely terminal degradation product .

Table 4.3 : ^{119}Sn Mössbauer Parameters of Dibutyltinbis-(isooctylthioglycollate) and its Degradation Products in the Pure State and when dispersed in PVC (at 1.2% (w/w)) at 80K

Sample	δ (mms^{-1})	Δ mms^{-1}	Γ mms^{-1}
Bu$_2$Sn(IOTG)$_2$ Pure	1.46	2.29	0.89
Bu$_2$Sn(IOTG)$_2$ in PVC (milled)	1.48	2.30	0.95
Bu$_2$SnCl(IOTG) Pure	1.43	2.95	0.94
Bu$_2$SnCl(IOTG) in PVC (milled)	1.43	2.98	0.94
Bu$_2$SnCl$_2$ Pure	1.64	3.47	0.97
Bu$_2$SnCl$_2$ in PVC (solvent cast from dichloromethane)	1.50	3.02	0.94
Bu SnCl$_3$ Pure	1.30	1.91	1.03
Bu SnCl$_3$ in PVC (solvent cast from dichloromethane)	1.17	1.94	1.00
SnCl$_4$ Pure	0.82	–	1.32
SnCl$_4$ in PVC (solvent cast from dichloromethane)	0.30	–	1.24

Parameters ± 0.02 mms^{-1} for pure compounds and ± 0.05 mms^{-1} when dispersed in PVC

Table 4.4 : ^{119}Sn Mössbauer Parameters of Dibutyltinbis-(isooctylthioglycollate) and its Degradation Products in PVC (at 1.2% w/w) after an Exposure of 200 kGy at 80K

Sample	δ mms^{-1}	Γ mms^{-1}
Bu$_2$Sn(IOTG)$_2$ in PVC (milled)	0.36	1.02
Bu$_2$SnCl(IOTG) in PVC (milled)	0.31	1.02
Bu$_2$SnCl$_2$ in PVC (solvent cast from dichloromethane)	0.36	1.04
BuSnCl$_3$ in PVC (solvent cast from dichloromethane)	0.39	1.01
SnCl$_4$ in PVC (solvent cast from dichloromethane)	0.39	1.06

Parameters ± 0.05 mms^{-1}

4.3 CONCLUSIONS

The variable exposure study of dibutyltinbis-
(isooctylthioglycollate) [2] in PVC has shown that
complex mixtures of degradation products are present
at exposures between 1 and 100 kGy. The resulting
Mössbauer spectra could not be computer fitted as
Lorentzian lines with parameters corresponding to the
likely degradation products because of their complexity.
By analysis of the absorption line positions however,
rapid conversion of the stabiliser to the dibutylchlorotin
thioglycollate [5] and dibutyltin dichloride was indicated
at exposures up to 20 kGy. Formation of [5] was observed
in the infrared spectra of thin PVC films containing
the stabiliser [2] after exposure, and was found to be
present to a small extent after the 100 kGy exposure
(in solvent cast films).

The model irradiation study (Section 4.2.2) showed that
the stabiliser [2], dibutylchlorotin thioglycollate [5],
dibutyltin dichloride and butyltin trichloride are
converted to stannic chloride in PVC after exposure to
irradiation. These results are consistent with the
proposed degradation scheme for stabilisers [1], [2]
and [3].

The results obtained in the variable exposure study
differ from those expected from thermal degradation
of this system where conversion to the dibutylchlorotin
thioglycollate or dibutyltin dichloride are anticipated.[6,7]

However, the photochemical study by Brooks et al[8] of PVC containing dibutyltinbis(isooctylthioglycollate) [2] did show some similarity with these irradiation studies since a degradation product with Mössbauer parameters close to those found for stannic chloride in irradiated PVC was identified. This degradation product was mistakenly identified as stannic oxychloride but is likely to have been stannic chloride.

4.4 REFERENCES

1. Report of the Joint FAO/IAEA/WHO Expert Committee, WHO Technical Report Series, 1981, No 659.

2. B.W. Rocket, M. Hadlington and W.R. Poyner, J. Appl. Polym. Sci., 1974, 18, 745.

3. T. Van Hoang, A. Michel and A. Guyot, Polym. Deg. and Stab., 1982, 4, 213.

4. V. Bellenger, J. Verdu, L.B. Carette, Z. Wymalalova and Z. Vymazil, Polym. Deg. and Stab., 1982, 4, 303.

5. P.B. Cooray, Polym. Deg. and Stab., 1984, 7, 1.

6. D.W. Allen, J.S. Brooks, R.W. Clarkson, M.T.J. Mellor and A.G. Williamson, J. Organometal. Chem., 1980, 199, 299.

7. A.H. Frye, R.W. Horste and M.A. Paliobagis, J. Polym. Sci., A2, 1964, 1765.

8. J.S. Brooks, R.W. Clarkson, D.W. Allen, M.T.J. Mellor and A.G. Williamson, Polym. Deg. and Stab., 1982, 4, 359.

CHAPTER 5 : EXTRACTION AND ANALYSIS OF DEGRADATION PRODUCTS FROM IRRADIATED POLY(VINYLCHLORIDE) CONTAINING ORGANOTIN STABILISERS

5.1   INTRODUCTION

5.2   RESULTS AND DISCUSSION

5.2.1   MODEL EXTRACTION STUDIES

5.2.2   EXTRACTION STUDIES OF IRRADIATED POLY(VINYL-CHLORIDE) CONTAINING DIBUTYLTINBIS(ISOOCTYL-THIOGLYCOLLATE) AND DIBUTYLTINBIS(ISOOCTYL-MALEATE)

5.3   CONCLUSIONS

5.4   EXPERIMENTAL

5.5   REFERENCES

5.1 INTRODUCTION

In Chapters 3 and 4 it has been shown that when PVC
containing dioctyltinbis(isooctylthioglycollate) [1],
dibutyltinbis(isooctylthioglycollate) [2] and
dibutyltinbis(isooctylmaleate) [3] is exposed to high
doses of irradiation, up to 200 kGy, the tin-moiety of
each of the stabilisers is converted eventually to stannic
chloride. The variable exposure study (Section 4.2) of
PVC containing dibutyltinbis(isooctylthioglycollate) [2]
for exposures between 1 and 100 kGy has revealed complex
mixtures of degradation products in the Mössbauer spectra
which could not be computer fitted to obtain their
identity. Model irradiation studies (Section 4.2.2)
using the proposed degradation products of [2] have
indicated the route of degradation during irradiation.
Infrared spectra of PVC films (Section 4.2.1) containing
this stabiliser [2] show that dibutylchlorotin
thioglycollate [5] is formed in the initial stages of the
degradation process during irradiation.

Due to the complexity of the Mössbauer spectra obtained
in the variable exposure study, conclusive structural
detail of all the degradation products could not be
obtained. Therefore, to substantiate the degradation
pathway for the stabilisers (Section 3.3) and obtain
quantitative information about the conversion to the
degradation products at specific exposures, alternative
chemical procedures were sought. The selective

quantitative determination of mixtures of alkyltin compounds can be carried out by gas chromatographic separation.[1-4] Mixtures of partially alkylated tin compounds may undergo disproportionation on heating, so direct chromatographic separation is unreliable.[5] This difficulty can be overcome by alkylation of the mixture with an appropriate Grignard reagent. For example, a mixture of Bu_nSnY_{4-n} ($Y = SCH_2CO_2C_8H_{17}$, $O_2CCH=CHCO_2C_8H_{17}$ or Cl) compounds is converted to a mixture of Bu_nSnR_{4-n} species (R = alkyl) which can be quantitatively separated by gas chromatography.[1,2] Rocket et al[4] have extracted organotin chlorides and stannic chloride from thermally degraded PVC and analysed them by gas chromatography after conversion to n-propyltin derivatives by reaction with the Grignard reagent, n-propylmagnesium chloride.

For the stabilisers [2] and [3] and their degradation products, this would mean conversion to dibutyl-di-n-propyl-, butyl-tri-n-propyl and tetra-n-propyl stannanes as shown below:

(i) Bu_2SnY_2 $\xrightarrow{\text{n-PrMgCl}}$ $Bu_2Sn^nPr_2$ (1)

(ii) Bu_2SnYCl $\xrightarrow{\text{n-PrMgCl}}$ $Bu_2Sn^nPr_2$ (2)

(iii) Bu_2SnCl_2 $\xrightarrow{\text{n-PrMgCl}}$ $Bu_2Sn^nPr_2$ (3)

(iv) $BuSnCl_3$ $\xrightarrow{\text{n-PrMgCl}}$ $BuSn^nPr_3$ (4)

(v) $SnCl_4$ $\xrightarrow{\text{n-PrMgCl}}$ Sn^nPr_4 (5)
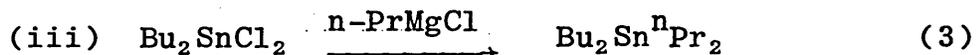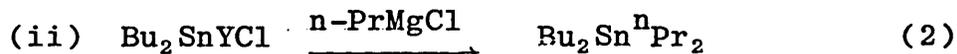
This technique, however, does not differentiate between the degradation products involved in reactions (1) - (3) since all are converted to dibutyldi-n-propylstannane. A reliable estimate of the quantities of these degradation products will therefore be difficult to obtain due to the ligand exchange reactions which occur rapidly in solution at room temperature[6,7] as shown in reaction (6):

$$Bu_2Sn(IOTG)_2 + Bu_2SnCl_2 \rightleftharpoons 2Bu_2SnCl(IOTG) \qquad (6)$$
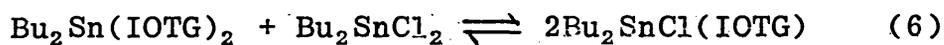
Similar exchange reactions have been postulated between $BuSnCl_3$ and $Bu_2Sn(IOTG)_2$ in solution[6,8] and various $BuSnCl_{3-n}(IOTG)_n$ derivatives could possibly occur within the PVC. These will be ultimately converted to butyltin trichloride and stannic chloride during irradiation and will be identified by chromatographic analysis.

Samples of PVC containing the stabilisers [2] and [3] have been irradiated at various exposures up to 200 kGy and, after extraction of the degradation products, their relative concentrations obtained by gas chromatographic separation.

5.2 RESULTS AND DISCUSSION

5.2.1 Model Extraction Studies

Extraction of organotin compounds from polymers is usually carried out by soxhlet extraction with diethyl-ether.[9] Irradiated PVC samples containing dibutyltinbis(isooctylthioglycollate) [2] were soxhlet

extracted with diethylether for 100 hours. The super-
natant liquid was analysed for stannanes after treatment
with n-propylmagnesium chloride.

Figure 5.1 shows a chromatogram of a mixture of
dibutyl-di-n-propyl-, butyl-tri-n-propyl- and
tetra-n-propyl-stannanes in diethylether (1% w/v for
each stannane). The chromatogram shows good resolution
of the stannanes. Figure 5.2 shows the chromatogram
of an extract of irradiated PVC (milled) containing
dibutyltinbis(isooctylthioglycollate) [2] (at 1.2% (w/w))
after an exposure of 100 kGy. This chromatogram shows
clearly the presence of the alkylated degradation
products $Bu_2Sn^nPr_2$, $BuSn^nPr_3$ and Sn^nPr_4 corresponding
to degradation products Bu_2SnX_2 (where X = $SCH_2CO_2C_8H_{17}$
or Cl), $BuSnCl_3$ and $SnCl_4$ respectively, in the polymer.

Table 5.1 shows the chromatographic analysis of a series
of milled PVC samples containing dibutyltinbis(isooctyl-
thioglycollate) [2] after exposure of irradiation
up to 200 kGy. These results clearly show mixtures of
the expected degradation products and substantiate the
proposed degradation pathway of the stabiliser [2].
After the 200 kGy exposure, however, only 29% conversion
to stannic chloride was detected by gas chromatography,
the remaining tin being in a mono- or dibutyl-state.
This conflicts significantly with the Mössbauer spectrum
of this PVC sample which showed only one major component
(Figure 3.2.B) which corresponded to stannic chloride.

Figure 5.1   Chromatographic Separation of Stannane Standards $Bu_2Sn^nPr_2$, $BuSn^nPr_3$ and Sn^nPr_4 in Diethylether (1% w/v)

Sn^nPr_4

$BuSn^nPr_3$

$Bu_2Sn^nPr_2$

Injection
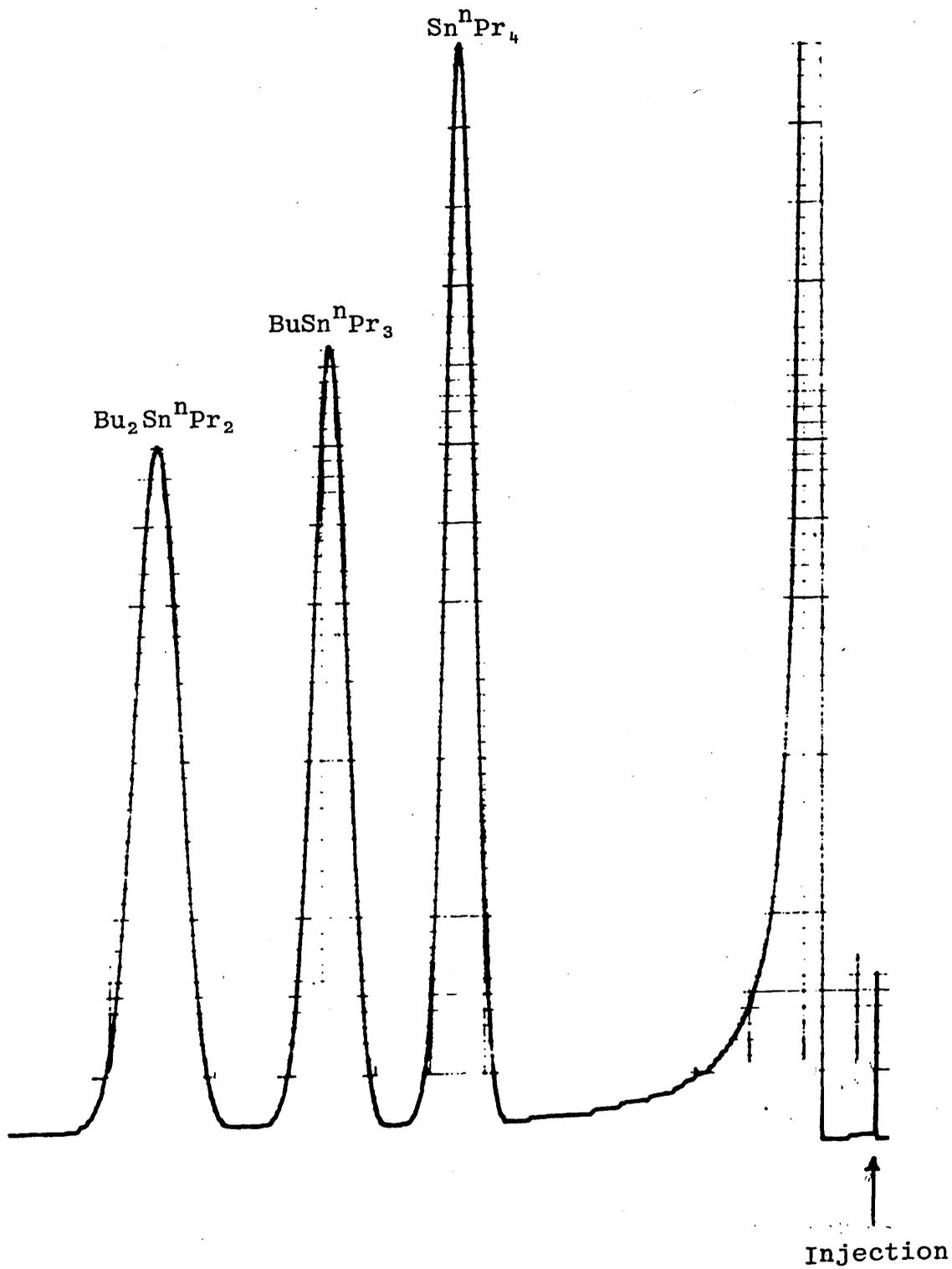
Figure 5.2 Chromatographic Separation of Propylated
           Degradation Products obtained from Irradiated
           PVC (milled) containing Dibutyltinbis(isooctyl-
           thioglycollate) after an Exposure of 100 kGy

Sn^nPr_4

$Bu_2Sn^nPr_2$

$Bu_3Sn^nPr_3$

Injection
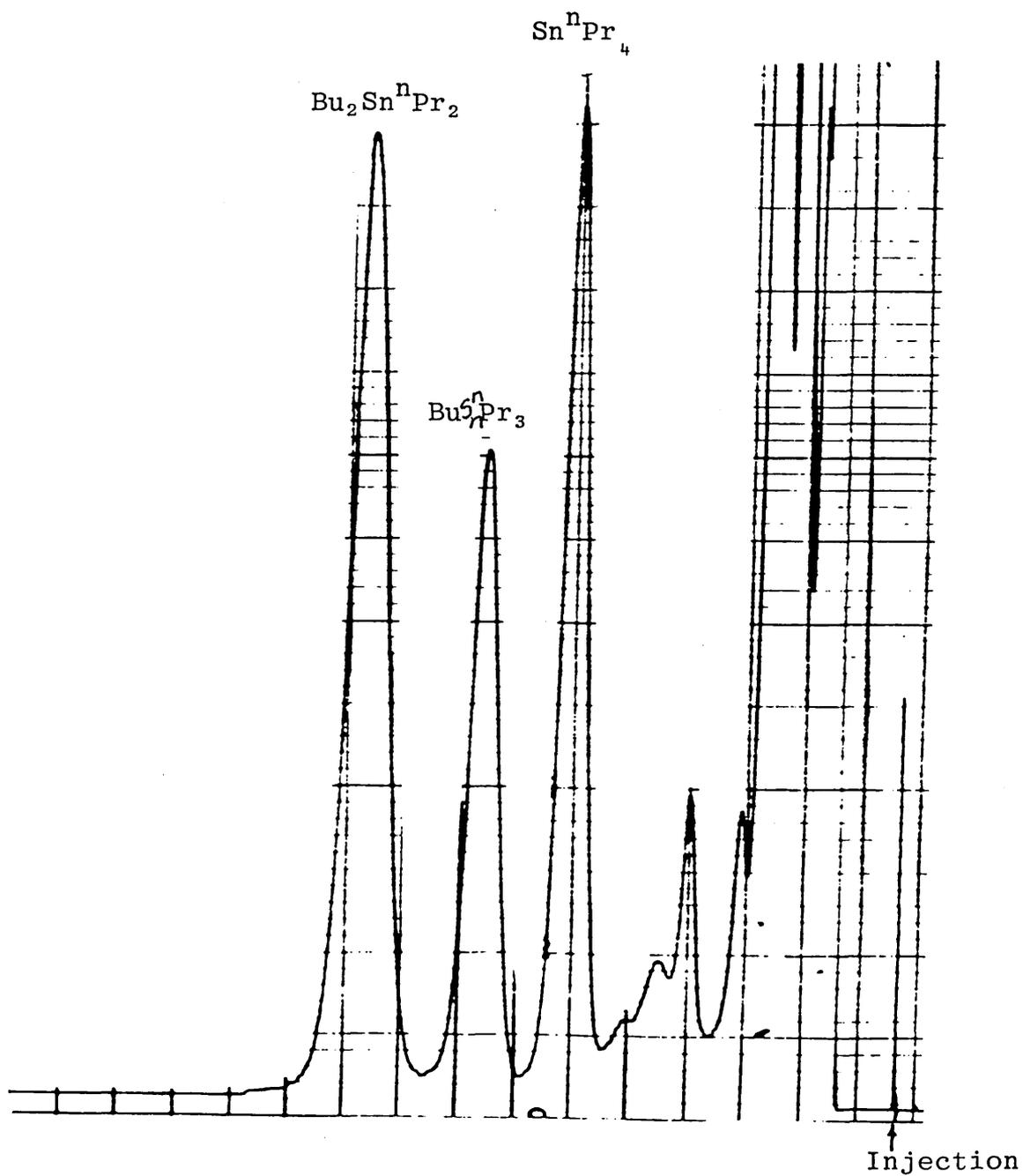
Table 5.1 : Chromatographic Analysis of Irradiated PVC
(milled) containing Dibutyltinbis(isooctyl-
thioglycollate) (1.2% (w/w)) after soxhlet
extraction with Diethylether

Exposure (kGy)	Relative Concentration of Degradation Product (%)		
	Bu_2SnX_2 [†]	$BuSnCl_3$	$SnCl_4$
0	94	6	<1
10	83	14	3
20	84	13	3
30	79	18	3
50	75	20	5
80	65	25	10
100	62	23	15
200	45	26	29

(† X = $SCH_2CO_2C_8H_{17}$ or Cl)

Table 5.2 : Chromatographic Analysis of PVC Samples
(solvent cast from dichloromethane) containing
a Mixture of Dibutyltin Dichloride, Butyltin
Trichloride and Stannic Chloride (at 1.2% w/w
for each compound) after Soxhlet Extraction
with Diethylether

Sample	Relative Concentration of Tin Compound Extracted (%)		
	Bu_2SnCl_2	$BuSnCl_3$	$SnCl_4$
1	1.00	1.02	0.40
2	1.00	1.04	0.53

Table 5.2 shows the chromatographic results for PVC samples containing a mixture (1.2% w/w for each compound) of dibutyltin dichloride, butyltin trichloride and stannic chloride (dispersed in PVC by solvent casting from dichloromethane) after soxhlet extraction with diethylether for 100 hours. The duplicate results show that stannic chloride is not extracted as efficiently as the organotin chlorides. The stannic chloride may be extracted even less efficiently in irradiated PVC samples due to its interaction with the polymer and could account for the unexpectedly low concentrations found from the analysis of irradiated PVC samples containing dibutyltinbis(isooctyl-thioglycollate) (Table 5.1). Stannic chloride is less soluble than the organotin compounds in diethylether due to the formation of an etherate complex , $SnCl_4(OEt_2)_2$,[10] which will make its extraction from the PVC more difficult. Therefore, in order to overcome these problems, it was decided that the degradation products must be liberated from the PVC by total dissolution of the polymer in tetrahydrofuran, as described by Rocket et al,[4] so as to ensure their quantitative removal from the PVC matrix.

5.2.2 Extraction Studies of Irradiated Poly(vinylchloride) Containing Dibutyltinbis(isooctylthioglycollate) and Dibutyltinbis(isooctylmaleate)

Samples of PVC containing the stabilisers [2] and [3] were exposed to irradiation doses up to 200 kGy. The samples were then dissolved in tetrahydrofuran and, after removal of the polymer and conversion of the stabiliser degradation products to their respective stannanes by the addition of n-propylmagnesium chloride, analysed by gas chromatography.

Table 5.3 shows the chromatographic analysis of irradiated milled PVC samples containing stabiliser [2] (at 1.2% (w/w)). The results show that, prior to irradiation, the milled samples contain a mixture of organotin compounds resulting from degradation which occurs in the milling process and some conversion to butyltin trichloride (6%) and stannic chloride (2%) is observed. This demonstrates the relative insensitivity of the Mössbauer technique to these species at low concentration since no significant change in Mössbauer parameters could be observed when the pure stabiliser was dispersed in PVC by milling. As the exposure is increased up to 20 kGy, the conversion to butyltin trichloride and stannic chloride is observed. After further exposure, the relative concentration of butyltin trichloride stays relatively constant (∿ 17%) even up to an exposure of 200 kGy. After the 100 kGy exposure, much of the stabiliser (47%) has been converted

Table 5.3 : Chromatographic Analysis of Irradiated PVC Samples (milled) containing Dibutyltinbis(isooctylthioglycollate) (1.2% (w/w))

Exposure (kGy)	Relative Concentration of Degradation Product (%)		
	Bu_2SnX_2 [†]	$BuSnCl_3$	$SnCl_4$
0	92	6	2
5	87	10	3
10	88	7	5
15	75	15	10
20	72	17	11
25	70	16	14
50	52	14	34
100	35	18	47
200	15	17	68

(† $X = SCH_2CO_2C_8H_{17}$ or Cl)

to stannic chloride. This value, although significantly higher than observed for the diethylether extraction of a similar sample (Table 5.1), is still much lower than might have been anticipated from the appearance of the Mössbauer spectrum which showed only one major component. This may indicate that the stannic chloride is preferentially detected with respect to the other degradation products in the Mössbauer experiment which could result from this compound having a substantially higher recoilless fraction than the other degradation products. After the 200 kGy exposure, the chromatographic analysis shows that the majority (68%) of the stabiliser [2] has been converted to stannic chloride.

For the corresponding solvent cast samples containing dibutyltinbis(isooctylthioglycollate) [2] (Table 5.4), the degradation process to stannic chloride is similarly observed. However, prior to irradiation, no dealkylation of the stabiliser is observed and the infrared spectrum of this sample shows no observable conversion to dibutyl-chlorotin thioglycollate [5]. The results for the solvent cast and milled samples show close similarity at exposures up to 10 kGy but after the 50 kGy exposure conversion to stannic chloride is much slower for the solvent cast sample (16%) than for the corresponding milled sample (34%). After further exposure, the conversion to stannic chloride remains significantly higher for the milled sample and for the 200 kGy exposure the conversion to stannic chloride is much higher (68%) than for the solvent cast sample (47%).

Table 5.4 : Chromatographic Analysis of Irradiated PVC
Samples (solvent cast from dichloromethane)
containing Dibutyltinbis(isooctylthioglycollate)
(1.2% (w/w))

Exposure (kGy)	Relative Concentration of Degradation Product)%)		
	Bu_2SnX_2 [†]	$BuSnCl_3$	$SnCl_4$
0	100	<1	<1
10	86	10	4
50	59	25	16
100	31	29	40
200	36	17	47

(† X = $SCH_2CO_2C_8H_{17}$ or Cl)

This may reflect the method of sample preparation and the milling process may accelerate the degradation process.

Table 5.5 shows the chromatographic results for irradiated milled PVC containing dibutyltinbis(isooctylthioglycollate) [2] at a higher stabiliser concentration (4% (w/w)). A greater stabilisation effect is observed, since after the 100 kGy exposure, the polymer remains transparent and the Mössbauer spectrum (Figure 5.3) clearly shows a multi-component spectrum which is substantially different from that observed at the lower stabiliser concentration (1.2% (w/w)) where only one major component is clearly observed. The computer fit to the Mössbauer spectrum in Figure 5.3, corresponding to a single line component representing stannic chloride and a doublet component representing the sum of Lorentzian lines of the remaining quadrupole doublet components, indicates that after the 100 kGy exposure much less (30%) conversion to stannic chloride has occurred. The chromatographic analysis of this sample again shows much less conversion (18%) than was estimated from the Mössbauer spectrum.

Table 5.6 shows the chromatographic results for irradiated milled PVC samples containing dibutyltinbis(isooctylmaleate) [3] (at 2% (w/w)). Some degradation of the stabiliser is again observed as a result of the milling process. The results show that, after increasing exposures, the stabiliser [3] is converted to stannic chloride, and

Table 5.5 Chromatographic Analysis of Irradiated PVC

Samples (milled) containing

Dibutyltinbis(isooctylthioglycollate)

(4% (w/w))

Exposure (kGy)	Relative Concentration of Degradation Product (%)		
	Bu_2SnX_2[†]	$BuSnCl_3$	$SnCl_4$
0	99	1	<1
10	86	9	5
50	70	18	12
100	57	25	18
200	35	18	47

(† X = $SCH_2CO_2C_8H_{17}$ or Cl)

Table 5.6 : Chromatographic Analysis of Irradiated PVC

Samples (milled) containing

Dibutyltinbis(isooctylmaleate) (2% (w/w))

Exposure (kGy)	Relative Concentration of Degradation Products (%)		
	Bu_2SnX_2[†]	$BuSnCl_3$	$SnCl_4$
0	97	3	<1
5	91	5	4
10	90	7	3
15	92	4	4
20	92	4	4
25	89	6	5
50	68	16	16
100	59	22	19
200	41	17	42

(† X = $O_2C.CH=CHCO_2C_8H_{17}$ or Cl)

Figure 5.3   Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC (milled)
(at 4% (w/w)) after an Exposure of 100 kGys recorded at 80K
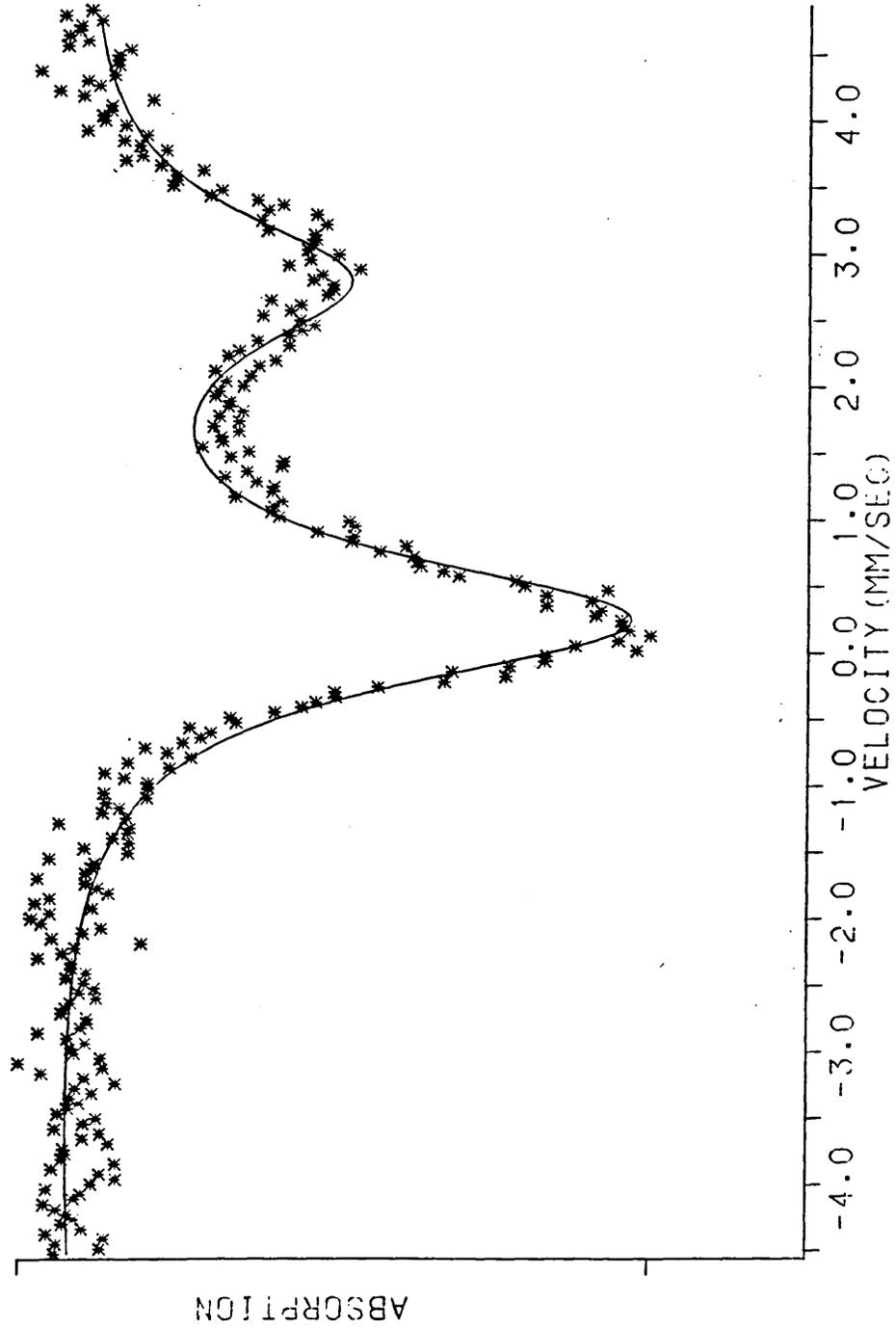
butyltin trichloride is an intermediate degradation
product showing that an identical degradation process
occurs for both the thioglycollate [1], [2] and maleate
[3] stabilisers during irradiation. Conversion of this
stabiliser [3] to stannic chloride takes place less
rapidly than the thioglycollate stabiliser [2]. After
an exposure of 50 kGy, much less conversion to stannic
chloride (16%) has occurred than for the thioglycollate
stabiliser (2) (34% at 1.2% (w/w) stabiliser concentra-
tion). A similar conversion to stannic chloride (12%)
was observed for the thioglycollate stabiliser [2]
at the much higher concentration (4% (w/w)). This
indicates that the thioglycollate stabilisers [1] and [2]
are more susceptible towards irradiation degradation
than the maleate stabiliser [3]. The maleate
stabiliser [3], although more resistant to degradation
on irradiation, did not, however, retard the
discolouration of the polymer as effectively as the
thioglycollate stabiliser [2] (at 4% (w/w)). The
thioglycollate stabiliser [2], having a strong antioxidant
effect, efficiently retards polyene formation by the
addition of thiolester groups ($HSCH_2CO_2C_8H_{17}$) across the
double bonds formed in the dehydrochlorination process.
After an exposure of 200 kGy, much less conversion to
stannic chloride (42%) was detected by chromatographic
analysis than was estimated from the Mössbauer spectrum
(80%) shown in Figure 3.5.B.

5.3 CONCLUSIONS

The results obtained for both thioglycollate [2] and
maleate stabilisers [3] show that an analogous
degradation process occurs during irradiation of PVC
stabilised by these compounds, ie

$$R_2SnY_2 \xrightarrow[(1)]{\gamma \cdot PVC} R_2SnYCl \xrightarrow[(2)]{\gamma \cdot PVC} R_2Sn \ Cl_2 \xrightarrow[(3)]{\gamma \cdot PVC}$$

$$RSnCl_3 \xrightarrow[(4)]{\gamma \cdot PVC} SnCl_4$$
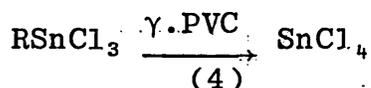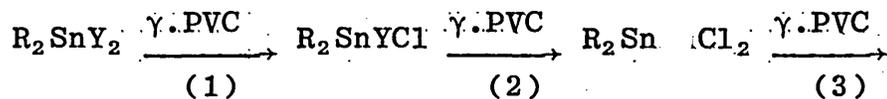
(R = Bu or Oct, Y = $SCH_2CO_2C_8H_{17}$ or

$O_2C \cdot CH{=}CHCO_2C_8H_{17}$)

The final degradation product, stannic chloride, is
associated with chlorine atoms of the polymer or hydrogen
chloride liberated during the degradation process. This
degradation product was not identified by other workers[11,12]
in similar irradiation studies of organotin-stabilised PVC
where the degradation products were extracted from the
PVC.

The chromatographic results have shown that dibutyltinbis-
(isooctylthioglycollate) [2] is converted to stannic
chloride more rapidly than is dibutyltinbis(isooctylmaleate)
[3] at exposures up to 200 kGy but the maleate stabiliser
[3] does not retard the formation of polyene sequences
correspondingly because of its weak antioxidant effect
with respect to the thioglycollate stabilisers [1] and [2].

The chromatographic studies of irradiated PVC containing the stabilisers [2] and [3] show much less conversion to stannic chloride than was estimated from the Mössbauer spectra of these samples. This suggests that stannic chloride (or its complexes in the polymer) may have an enhanced recoilless fraction in the PVC matrix compared to the other degradation species. This could result in an enhanced absorption area for stannic chloride leading to the anomalous results obtained from the chromatographic analyses of these irradiated PVC samples.

The chromatographic results also show that the milling process produces some stabiliser breakdown and low concentrations of butyltin trichloride and stannic chloride can be observed prior to the irradiation process for both thioglycollate [2] and maleate [3] stabilisers.

Increasing the concentration of the thioglycollate stabiliser [2] (to 4% (w/w)) results in an enhancement of the stabilisation towards the irradiation process. After 100 kGy exposure, the milled PVC remains transparent, though yellowed slightly, and much less conversion to stannic chloride is observed.

The results in Tables 5.3, 5.4, 5.5 and 5.6 at exposures up to 10 kGy (the exposure likely to be used in food irradiation applications), show that for the thioglycollate stabiliser [2] much of the stabiliser (88%) remains in the dialkyl state as the dibutylchlorotin thioglycollate [5] or dibutyltin dichloride (or undegraded stabiliser) in

milled PVC. Some conversion to butyltin trichloride and stannic chloride (7% and 5% respectively) is observed (Table 5.3). For the maleate stabiliser [3] at this exposure, some conversion to butyltin trichloride and stannic chloride (7% and 3% respectively) is also observed in milled PVC. At the higher stabiliser concentration (4% (w/w)) the thioglycollate stabiliser [2] shows a similar conversion to these two products (10% and 4% respectively).

5.4 EXPERIMENTAL

Preparation of Chromatographic Standards

The appropriate organotin chloride or stannic chloride (2g) was dissolved in diethylether (25 ml) and treated with n-propylmagnesium chloride solution (25 ml), prepared from n-propylchloride (39.3g, 0.50 mole) and magnesium (12.2g, 0.5 mole) in ether (250 ml). After 30 min at room temperature, the excess n-propylmagnesium chloride was decomposed by the addition of methanol. The filtered solution was reduced in volume and vacuum distilled to obtain the pure stannane. The purity of the stannanes was ensured by chromatographic analysis.

Detection and Analysis of Organotin Compounds and Stannic Chloride in PVC

The PVC samples (2g) were dissolved in tetrahydrofuran (50 ml) at room temperature. The solution was treated with n-propylmagnesium chloride solution (40 ml) and after 1 hr, the excess n-propylmagnesium chloride was decomposed

by the addition of methanol. The polymer was
precipitated by the further addition of methanol and the
filtered solution was reduced in volume to 2 ml. The
degradation products were separated by gas-liquid
chromatography on a 10 ft glass column packed with
10% SE30 on Celite, using a Pye Series GCV Chromatograph
at a temperature of 200°C. The relative concentrations
of the degradation products was determined by the
'cut and weigh' method.

5.5 REFERENCES

1. G. Neubert and H. O. Wirth, Z. Anal. Chem., 1975, 273, 19.

2. K. Figge, J. Koch and H. Lubba, J. Chromatog., 1977, 131, 317.

3. Y. Jitsu, N. Kudo, K. Sato and T. Teshima, Bunseki Kagaku, 1969, 18, 169.

4. B.W. Rocket, M. Hadlington and W.R. Poyner, J. Appl. Polym. Sci., 1974, 18, 745.

5. G. Ayrey and R.C. Poller, in 'Developments in Polymer Stabilisation', Ed. G. Scott, Applied Science, London, 1980, p 15.

6. S.J. Blunden, L.A. Hobbs, P.J. Smith, A.G. Davis and S. Beng Teo, J. Organometal. Chem., 1985, 282, 9.

7. R.G. Parker and C.J. Carmen, Am. Chem. Soc. Adv. Chem. Ser., 1978, 169, 363.

8. V. Bellenger, J. Verdu and L.B. Carette, Polym. Deg. and Stab., 1981, 3, 3.

9. A. Krause and A. Lange in 'Introduction to the Chemical Analysis of Plastics', Ed. J. Haslam, London Iliffe Books, 1965. p 163.

10. I.R. Beattie and L. Rule, J. Chem. Soc., 1964, 3267.

11. K. Figge and W. Freytag, Dtsch. Lebensm.-Rundsch., 1977, 73, 205.

12. G. Haesen, R. Depans, H. Van Tilbeurgh, B. Le Goff
and F. Lox, J. Ind. Irradiation Tech., 1983, 1, 259.

CHAPTER 6 : APPLICATION OF THE DEBYE MODEL OF SOLIDS TO VARIABLE TEMPERATURE MOSSBAUER DATA OF TWO ORGANOTIN STABILISER DEGRADATION PRODUCTS IN PVC

6.1 INTRODUCTION

It has been shown in Chapter 5 that the expected degradation products were identified by chromatographic analysis of irradiated PVC samples containing the thioglycollate and maleate stabilisers. However, for each stabiliser, the proportion of stannic chloride found by chemical derivatisation was much less than was indicated by Mössbauer spectra. After an exposed dose of 100 kGy, milled PVC containing 1.2% (w/w) dibutyltinbis(isooctylthioglycollate) [2] showed a spectrum with only one major component clearly visible. The chromatographic analysis of this sample showed only 47% conversion to stannic chloride and the greater part of the remaining tin was found in the dialkyl state. This indicated that the stannic chloride may be more sensitive to detection by the Mössbauer technique when held in the polymer matrix than the other degradation products and hence an enhanced signal for stannic chloride could dominate the spectrum. If stannic chloride has a greater recoilless fraction, under these conditions, than the other degradation products this will result in a greater absorption area with respect to the other degradation products.

An indication of the relative magnitude of the recoilless fractions for the degradation products can be obtained by applying the Debye model of solids to variable temperature Mössbauer data for the degradation products dispersed in PVC. Variable temperature data have therefore been

recorded for stannic chloride and dibutyltin dichloride
when dispersed in PVC individually to represent the types
of degradation products found in the PVC matrix.

6.2 RESULTS AND DISCUSSION

6.2.1 Determination of Optimum Absorber Thickness for PVC Absorbers

In order to obtain useful information from the variable
temperature Mössbauer data, it must be ensured that the
Mössbauer thickness, t, is directly proportional to A,
the absorption area. It has been shown in Section 2.3.3
that, for small absorber thickness, the absorption line
area is related to the Mössbauer thickness by:

$$A(t) \; \alpha \; \tfrac{1}{2}t \; \exp \; (-\tfrac{1}{2}t) \; [I_0(\tfrac{1}{2}t) + I_1(\tfrac{1}{2}t)] \qquad (6.1)$$

which is reduced to a first approximation to:

$$A(t) \; \alpha \; f_s t \; (1 - 0.25t + 0.0625t^2 + ...) \quad (6.2)$$

for $t \ll 5$.

Typical t values for organotin degradation products
dispersed in PVC at 4% (w/w) can be calculated from
equation (6.3):

$$t = \beta.n.f_a \; \sigma_0 \; X \qquad\qquad\qquad (6.3)$$

e.g. For dibutyltin dichloride

β = $\tfrac{1}{2}$ for a quadrupole doublet
σ_0 = $1.403 \times 10^{-18} cm^2$
n = number of resonant nuclei/cm^2
X = number of layers of PVC sample.

To calculate n:

Mass of Bu_2SnCl_2 in PVC sample = 0.629 mg/cm^2
(one film layer)

$\therefore$ Mass of ^{119}Sn in PVC sample = 0.021 mg/cm^2

$\therefore$ Number of ^{119}Sn nuclei   = 1.063 x 10^{17} per layer
of PVC

$\therefore$ $t = \frac{1}{2}$ x 1.063 x 10^{17} x f_a x 1.403 x 10^{-18}

$\therefore$ $t = f_a$ (0.075) per layer of PVC

The recoilless fraction for Bu_2SnCl_2 in PVC at 4% (w/w)
is unknown but typical values for organotin compounds
occur in the range 0.06 to 0.40 at 80K.

If f_a = 0.06 :

t = 0.075 x 0.06 = 0.005 per film layer

$\therefore$ for 6 layers used $\underline{t = 0.030}$.

If f_a = 0.40 :

t = 0.40 x 0.075 = 0.03 per film layer

$\therefore$ for 6 layers $\underline{t = 0.180}$.

When t = maximum possible value of 0.180:

$A(t) \alpha \ f_s$ (0.180 - 0.008)

Any further terms can be considered negligible.

This represents a maximum possible error of < 5% and
therefore the area under the absorption peak can be
taken to be proportional to the absorber recoilless
fraction within an acceptable error.   If $A(t) \alpha t$ is

assumed for the PVC samples containing the degradation products, it should be possible to obtain values for f_a for stannic chloride and dibutyltin dichloride in PVC at 80K (at 4% w/w).

6.2.2 The Debye Model

The temperature dependence of the recoilless fraction is given by the Debye model of solids by an expression of the form[1]:

$$f_a(T) = \exp \frac{-3E_R}{2k_B\Theta_D} \left[1 + 4 \left\{ \frac{T}{\Theta_D} \right\}^2 \int_0^{\Theta_D/T} \frac{x\,dx}{e^x - 1} \right] \quad (6.4)$$

where $E_R = \dfrac{E_\gamma^2}{2\,M_{eff}\,C^2}$, Θ_D is the Debye temperature and M_{eff} is the effective vibrating mass.

In the high temperature limit ($T > \Theta_D$) the integral goes to Θ_D/T and hence

$$f_a(T) = \exp \left[\frac{-3E_R}{2k_B\Theta_D} - \frac{6E_R T}{k_B\Theta_D^2} \right] \quad (6.5)$$

Therefore for an ideal monatomic isotropic cubic solid, the slope of the $\ln f_a(T)$ versus T graph would be given by:

$$\frac{d(\ln f_a(T))}{dT} = \frac{-6E_R}{k_B\Theta_D^2} \quad (6.6)$$

and hence

$$\frac{d(\ln A)}{dT} = \frac{-3E_\gamma^2}{(M_{eff}\,C^2)\,k_B\Theta_D^2} \quad (6.7)$$

Equation (6.7) contains two unknowns, namely the Debye temperature, Θ_D, and the effective vibrating mass, M_{eff}, of the absorbing unit. Since we have no way of determining the true M_{eff} of stannic chloride and dibutyltin dichloride in the irradiated PVC matrix, it must be assumed to be the relative molecular mass of the compound. This leaves only Θ_D, the characteristic temperature, which is related to the strength of the binding of the absorbing unit in the PVC matrix unknown.

Tables 6.1 and 6.2 show the variable temperature Mössbauer absorption line area data over the temperature range 12K - 75K for PVC containing 4% (w/w) of stannic chloride and dibutyltin dichloride respectively. The values for the normalised line areas, A, were obtained by evaluating:

$$\text{Area} = \Gamma_H \times \frac{(\text{Background counts} - \text{counts at absorption peak})}{\text{Background Counts}} \times 100$$

for each absorption peak.

(Γ_H = Experimental full width of the absorption line at half height)

The resulting plots of lnA versus T for stannic chloride and dibutyltin dichloride in PVC at 4% (w/w) are shown in Figures 6.1 and 6.2 respectively. The linear regions on each of the slopes occur above the low temperature curvature as predicted by the Debye model and below any high temperature curvature caused by the anharmonic oscillation of the lattice.

- 190 -

Table 6.1 : Variable Temperature Mossbauer Absorption Line Areas for 4% (w/w) stannic chloride in PVC recorded over a temperature range of 12K - 75K

T(K)	A	ln(100A)
12	0.276	3.319
20	0.265	3.278
25	0.248	3.210
35	0.212	3.054
45	0.200	2.994
50	0.189	2.942
60	0.165	2.800
65	0.158	2.759
75	0.133	2.590

Table 6.2 : Variable Temperature Mössbauer Absorption Line Areas for 4% (w/w) dibutyltin dichloride in PVC recorded over a temperature range of 12K - 75K

T(K)	A	ln(100A)
12	0.122	2.502
20	0.110	2.400
25	0.102	2.320
35	0.075	2.016
45	0.061	1.806
50	0.053	1.664
60	0.041	1.431
65	0.034	1.210
75	0.023	0.818

Figure 6.1 Variation of Mössbauer Absorption Line Area with Temperature for Stannic Chloride in PVC
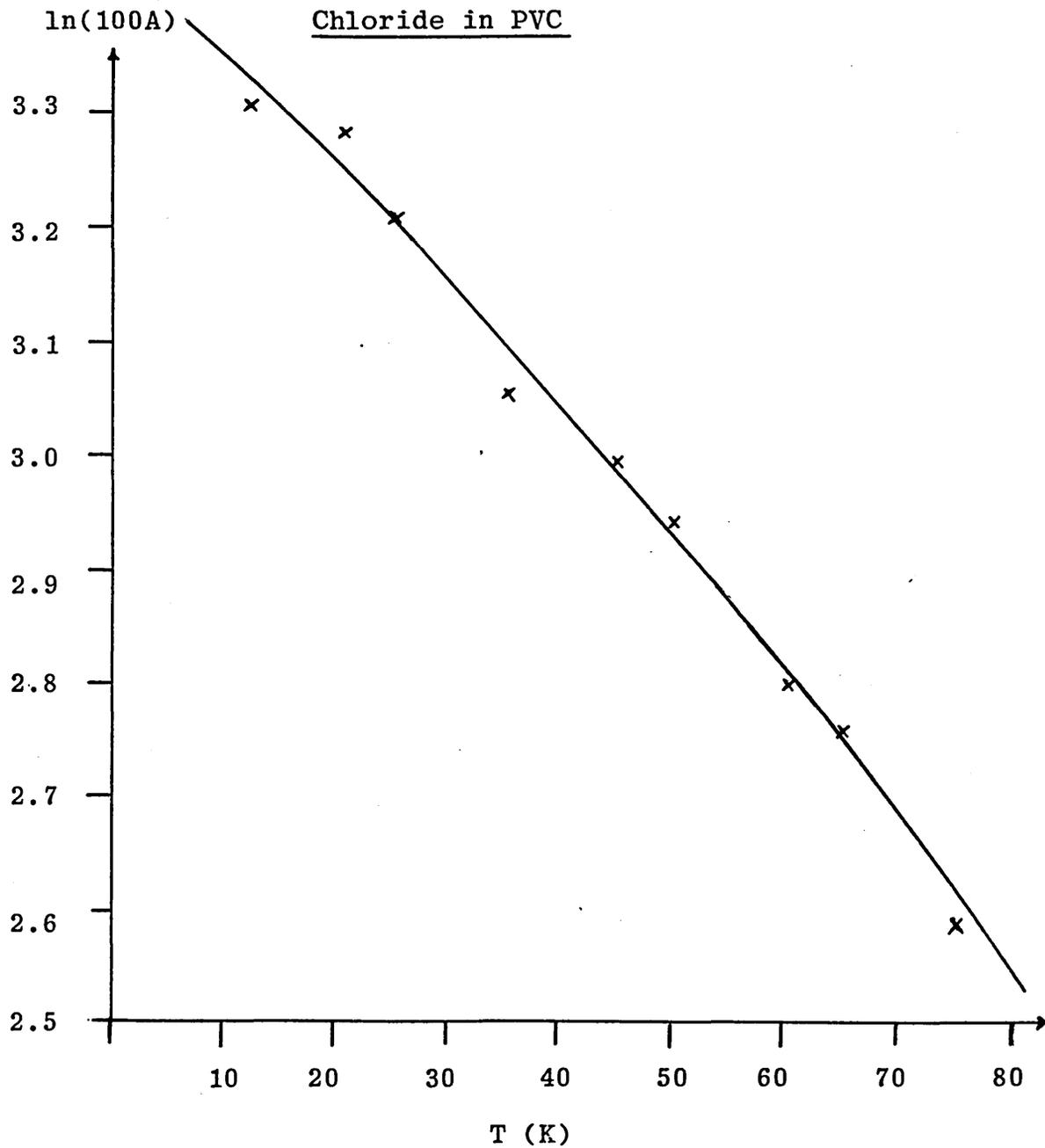
Figure 6.2   Variation of Mössbauer Absorption Line
Area with Temperature for Dibutyltin
Dichloride in PVC
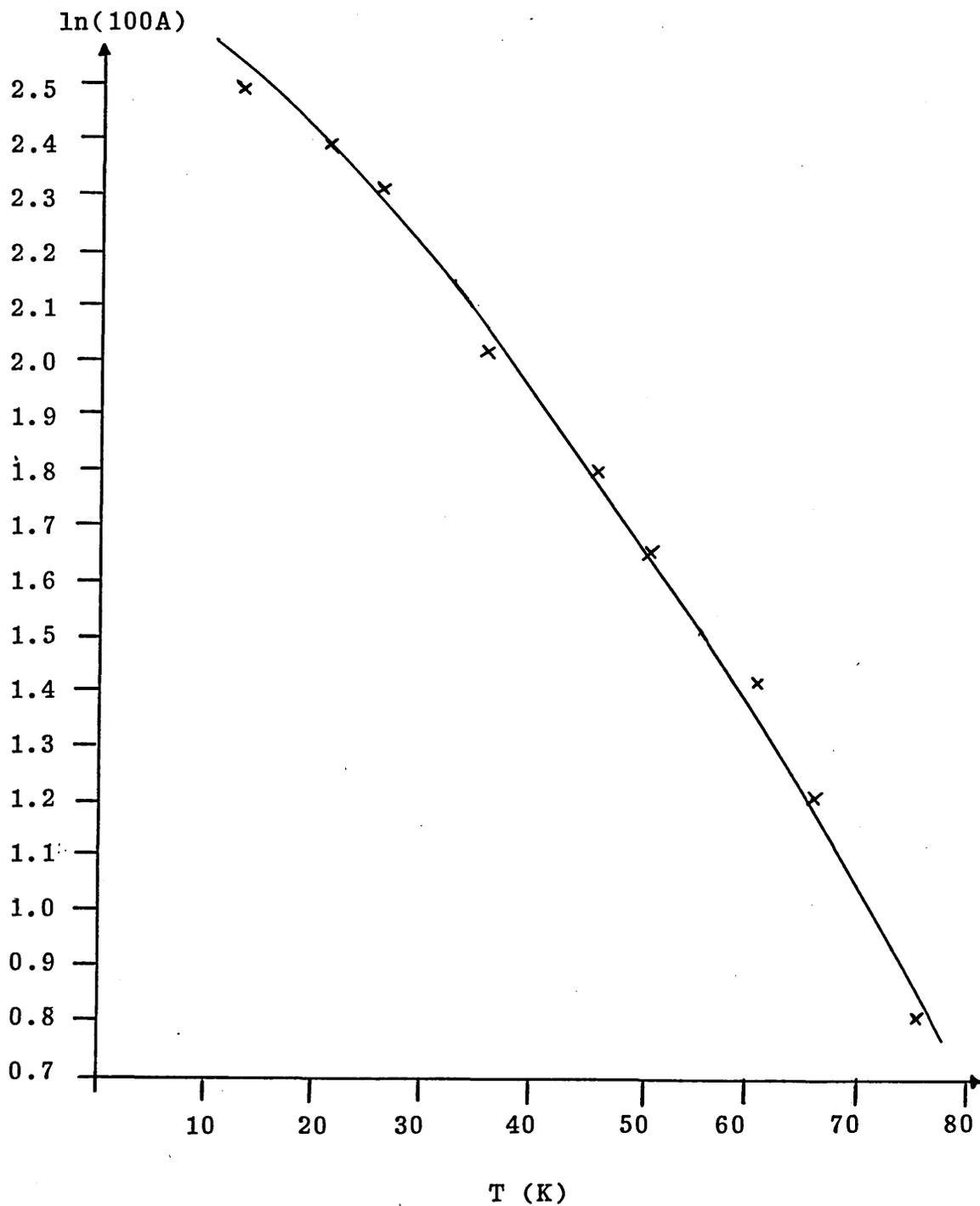
Using the gradients of these slopes, a value of Θ_D for each compound in the PVC matrix can be obtained from equation (6.7) and the recoilless fractions at 80K in the high temperature limit can be calculated from:

$$f_a = \exp\left[\frac{-3E_R}{k_B\,\Theta_D}\quad \frac{1}{2} - \frac{2T}{\Theta_D}\right] \qquad (6.8)$$

Substituting for E_R gives:

$$f_a = \exp\left[\frac{-3E_\gamma^2}{2\,M_{eff}\,C^2\,k_B\,\Theta_D}\left(\frac{1}{2} - \frac{2T}{\Theta_D}\right)\right] \qquad (6.9)$$

6.2.3 Calculation of Θ_D, E_R and f_a for Stannic Chloride and Dibutyltin Dichloride in PVC

1. FOR STANNIC CHLORIDE

$$\frac{d(\ln A)}{dT} = \frac{-3E_\gamma^2}{M_{eff}\,C^2\,k_B\,\Theta_D^2} \qquad (6.7)$$

$$\frac{d(\ln A)}{dT} = \text{Gradient of slope} = 0.012\ K^{-1}$$

M_{eff} = Relative Molecular Mass of stannic chloride = 260.5u   (1u = 931.5 MeV)

E_γ = 23.875 keV

k_B = 1.381 x 10^{-23} J K^{-1}

Substituting into (6.7) and rearranging gives:

$$\Theta_D^2 = \frac{3 \times (23.875 \times 10^3)^2 \times 1.6 \times 10^{-19}}{1.2 \times 10^{-2} \times 260.5 \times 931.5 \times 10^6 \times 1.381 \times 10^{-23}}$$

$$\Theta_D^2 = \frac{2.736 \times 10^{-10}}{4.021 \times 10^{-14}}$$

$$\Theta_D^2 = 6.804 \times 10^3$$

$$\Theta_D = 83K$$

To determine E_R :

$$E_R = \frac{E_\gamma^2}{2 M_{eff} C^2}$$

$$E_R = \frac{(23.875 \times 10^3)^2}{2 \times 260.5 \times 931.5 \times 10^6}$$

$$E_R = 1.175 \times 10^{-3} \ eV$$

Therefore, substituting into (6.9):

$$f_a(T) = \exp\left[\frac{-3E_\gamma^2}{2 M_{eff} C^2 K_B}\left(\frac{1}{2\Theta_D} - \frac{2T}{\Theta_D^2}\right)\right] \qquad (6.9)$$

$T = 80K$, $\Theta_D = 83K$, $E_R = 1.175 \times 10^{-3}$ eV

$$f_a(80) = \exp\left[\frac{-3 \times 1.175 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}}\right.$$
$$\left. \times \left(\frac{1}{166} + \frac{160}{(83)^2}\right)\right]$$

$$f_a(80) = \exp[-40.870 \times (0.029)]$$

$$f_a(80) = \exp(-1.185)$$

$$f_a(80) = 0.31$$

2. SIMILARLY FOR DIBUTYLTIN DICHLORIDE

$$\frac{d(\ln A)}{dT} = 0.026 \ K^{-1}$$

$$M_{eff} = 305.2$$

Substituting into (6.7) and rearranging:

$$\Theta^2_D = \frac{3 \times (23.875 \times 10^3)^2 \times 1.6 \times 10^{-19}}{2.6 \times 10^{-2} \times 305.2 \times 931.5 \times 10^6 \times 1.381 \times 10^{-23}}$$

$$\Theta^2_D = \frac{2.89 \times 10^{-10}}{1.021 \times 10^{-13}}$$

$$\Theta^2_D = 2.831 \times 10^3$$

$$\underline{\Theta_D = 53K}$$

To determine E_R :

$$E_R = \frac{(23.875 \times 10^3)^2}{2 \times 305.2 \times 931.5 \times 10^6} \ eV$$

$$\underline{E_R = 1.003 \times 10^{-3} \ eV}$$

Substituting into (6.9):

$$T = 80K, \ \Theta_D = 53K, \ E_R = 1.003 \times 10^{-3} \ eV$$

$$f_a(80) = \exp\left[\frac{-3 \times 1.003 \times 10^{-3} \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}}\left(\frac{1}{104} + \frac{160}{(53)^2}\right)\right]$$

$$f_a(80) = \exp[-34.887 \times (0.067)]$$

$$f_a(80) = \exp(-2.337)$$

$$\underline{f_a(80) = 0.10}$$

Table 6.3 summarises the lattice dynamics parameters calculated for stannic chloride and dibutyltin dichloride in PVC (at 4% (w/w)) at 80K.

Table 6.3 Mossbauer and Lattice Dynamics Parameters
          for Stannic Chloride and Dibutyltin Dichloride
          in PVC at 4% (w/w) at 80K

Compound	M_{eff} (u)	$\frac{d(\ln A)}{dT}$ (K^{-1})	Θ_D (K)	E_R (eV)	$f_a(T)$	Sensitivity Ratio $\frac{f_a(T)SnCl_4}{f_a(T)Bu_2SnCl_2}$
Stannic Chloride	260.5	1.2×10^{-2}	83	1.175×10^{-3}	0.31	3.1
Dibutyltin dichloride	305.2	2.6×10^{-2}	53	1.003×10^{-3}	0.10	1

The Debye temperatures, obtained from the experimental data for stannic chloride and dibutyltin dichloride in PVC, of 83K and 53K respectively, are significantly different in magnitude and indicate an appreciable difference in the strength of binding of the two compounds in the PVC matrix. The computed values for the recoilless fractions for these two compounds in PVC show that stannic chloride is a factor of 3.1 times more sensitive than dibutyltin dichloride to the Mössbauer technique at 80K. The resulting absorption area for stannic chloride will be subsequently 3.1 times greater than for dibutyltin dichloride at equal concentrations under these conditions.

This striking feature may well explain why the Mössbauer spectra of irradiated PVC samples are dominated by a single line component when clearly, as found from chemical derivatisation experiments, large concentrations of other degradation products still remain. These degradation products are likely to have similarly low recoilless fractions as dibutyltin dichloride in PVC. Table 6.4 shows the Mössbauer and lattice dynamics parameters for pure stannic chloride and dibutyltin dichloride at 80K. The parameters for stannic chloride were calculated from the data presented by Herber and Leahy[2], but those for dibutyltin dichloride were determined experimentally as before for PVC samples containing stannic chloride and dibutyltin dichloride. Table 6.5 shows the variable temperature Mössbauer absorption line area data over the temperature range 12K - 75K for pure dibutyltin dichloride. The resulting plot of lnA versus T is shown in Figure 6.3.

The recoilless fractions for pure stannic chloride and dibutyltin dichloride at 80K are 0.23 and 0.20 respectively. When dispersed in PVC (Table 6.3), significant changes in recoilless fraction occur for both compounds. That of stannic chloride increases from 0.23 to 0.31. This may result from the stannic chloride interacting with either hydrogen chloride liberated from the PVC, since it is known to be a prodegradant of PVC[3], or from interaction with chlorine atoms still attached to the polymer. This could result in the

stannic chloride becoming six—coordinate. Many six-coordinate complexes of stannic chloride show recoilless fractions close to that observed for stannic chloride in PVC[4].

Table 6.4 : Mössbauer and Lattice Dynamics Parameters
for Pure Stannic Chloride and Dibutyltin
Dichloride at 80K

Compound	M_{eff} (u)	$\dfrac{d(\ln A)}{dT}$ (K^{-1})	Θ_D (K)	E_R (eV)	$f_a(T)$	Sensitivity Ratio $\dfrac{f_a SnCl_4}{f_a Bu_2 SnCl_2}$
Stannic Chloride (Reference 2)	260.5	1.48×10^{-2}	74	1.175×10^{-3}	0.23	1.15
Dibutyltin Dichloride This work.	305.2	1.71×10^{-2}	64	1.002×10^{-3}	0.20	1

Table 6.5   Variable Temperature Mössbauer Absorption
Line Areas for Pure Dibutyltin Dichloride over
a temperature range of 12K - 75K

T(K)	A	$\ln(100A)$
12	0.080	2.073
20	0.075	2.016
25	0.071	1.958
35	0.061	1.813
45	0.051	1.635
50	0.048	1.575
60	0.039	1.370
65	0.037	1.304
75	0.029	1.066

Figure 6.3 Variation of Mössbauer Absorption Line
Area with Temperature for Pure Dibutyltin
Dichloride
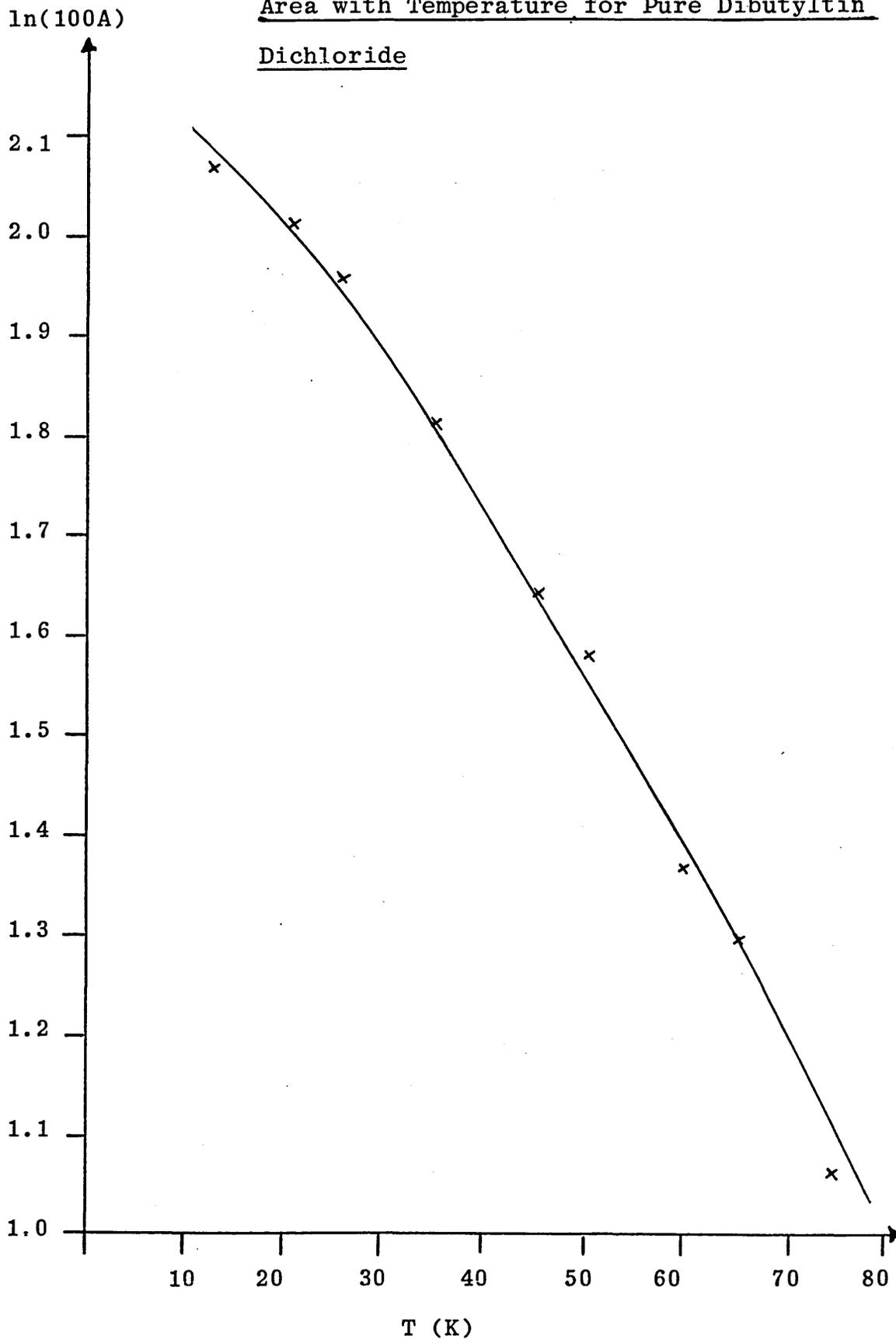
For dibutyltin dichloride, the situation is reversed and an appreciable drop in the recoilless fraction occurs from 0.20 in the pure state to 0.10 when dispersed in PVC. A Mössbauer study of the structural properties of dibutyltin dichloride when dispersed in PVC has been carried out by Brooks et al[5]. They proposed that the change in the magnitude of the quadrupole splitting observed for dibutyltin dichloride dispersed in PVC at 1.2% (w/w) from that of the pure material suggested a structural change from six—coordinate in the pure state to five—coordinate in PVC. Partial quadrupole splitting calculations were carried out for the possible structures which dibutyltin dichloride may adopt when diluted in an inert matrix. The results showed that, at low concentrations of dibutyltin dichloride dispersed in PVC, a dimeric five—coordinate structure is observed. This structural change also occurred when the dibutyltin dichloride was dispersed in a non-halogenated polymer such as polystyrene.

This structural change may also account for the fall in recoilless fraction when dibutyltin dichloride is dispersed in PVC. If the undegraded stabiliser and subsequent degradation products have equally low recoilless fractions as dibutyltin dichloride when dispersed in PVC, it is reasonable to assume that moderately low concentrations of stannic chloride will dominate the appearance of Mössbauer spectra when a mixture of components is present in the irradiated PVC samples.

6.3 CONCLUSIONS

Variable temperature Mössbauer data have shown that
stannic chloride and dibutyltin dichloride have
substantially different interactions with the PVC
matrix. Stannic chloride shows an increase in recoilless
fraction when dispersed in PVC compared to its pure
state, whereas the early degradation product, dibutyltin
dichloride, shows a marked decrease in recoilless
fraction when dispersed in PVC, probably due to the
breakdown of its polymeric structure [5].

The high recoilless fraction for stannic chloride when
dispersed in PVC accounts for Mössbauer spectra of
irradiated samples showing only one major degradation
product when clearly others are present.

Application of the Debye model to the variable
temperature Mössbauer data has revealed the complex
interactions which occur between organotin-stabiliser
degradation products and PVC which have led to the
difficulty in interpretation of the Mössbauer spectra
of irradiated PVC samples containing organotin stabilisers.

6.4 EXPERIMENTAL

The low temperatures required to cool the PVC samples were obtained by using an Air Products Cryogenic Refrigeration System (Figure 6.4). The CS-202 Expander Module used in conjunction with the DMX-20 interface is designed for applications in which the sample area must be isolated from all vibrations (i.e. to observe the Mössbauer effect).

The CS-202 Expander Module is a two-stage cryogenic refrigerator using gaseous helium as the refrigerant. Power to operate the expander module is drawn from and controlled by a compressor module which also supplies the required gaseous helium. Figure 6.5 is a simplified diagram identifying the key elements by which the expander module produces refrigeration.

During operation, the compressor module continuously draws low pressure helium from the system return line, compresses and cools it, then delivers it at high pressure through the system supply line to the refrigeration module.

The cryogenic system is designed such that the valve motor assembly and the cylinder assembly are mounted independently. These two parts are only directly coupled by a rubber bellows and the exchange gas. The two parts are held rigidly in precise alignment by external steel framework.

Figure 6.4   Air Products Cryogenic Refrigeration System

VACUUM SHROUD MODEL DMX-20
MOSSBAUER

DISPLEX MODEL CS-202

Spacer Screws

Tapped Holes for
Mounting
(1/4-20NC Thd's)

VACUUM
PUMPOUT

12°K to 300°K
SAMPLE AREA

Displex Mounting Flange

SET-UP SPACER (1 of 2 Pieces Shown)
(REMOVED DURING
OPERATION)

VIBRATION ISOLATION
BELLOWS

Vacuum Shroud Mounting
Flange

GAS TRANSFER HEAT
EXCHANGERS

RADIATION SHIELD

BERYLLIUM WINDOW
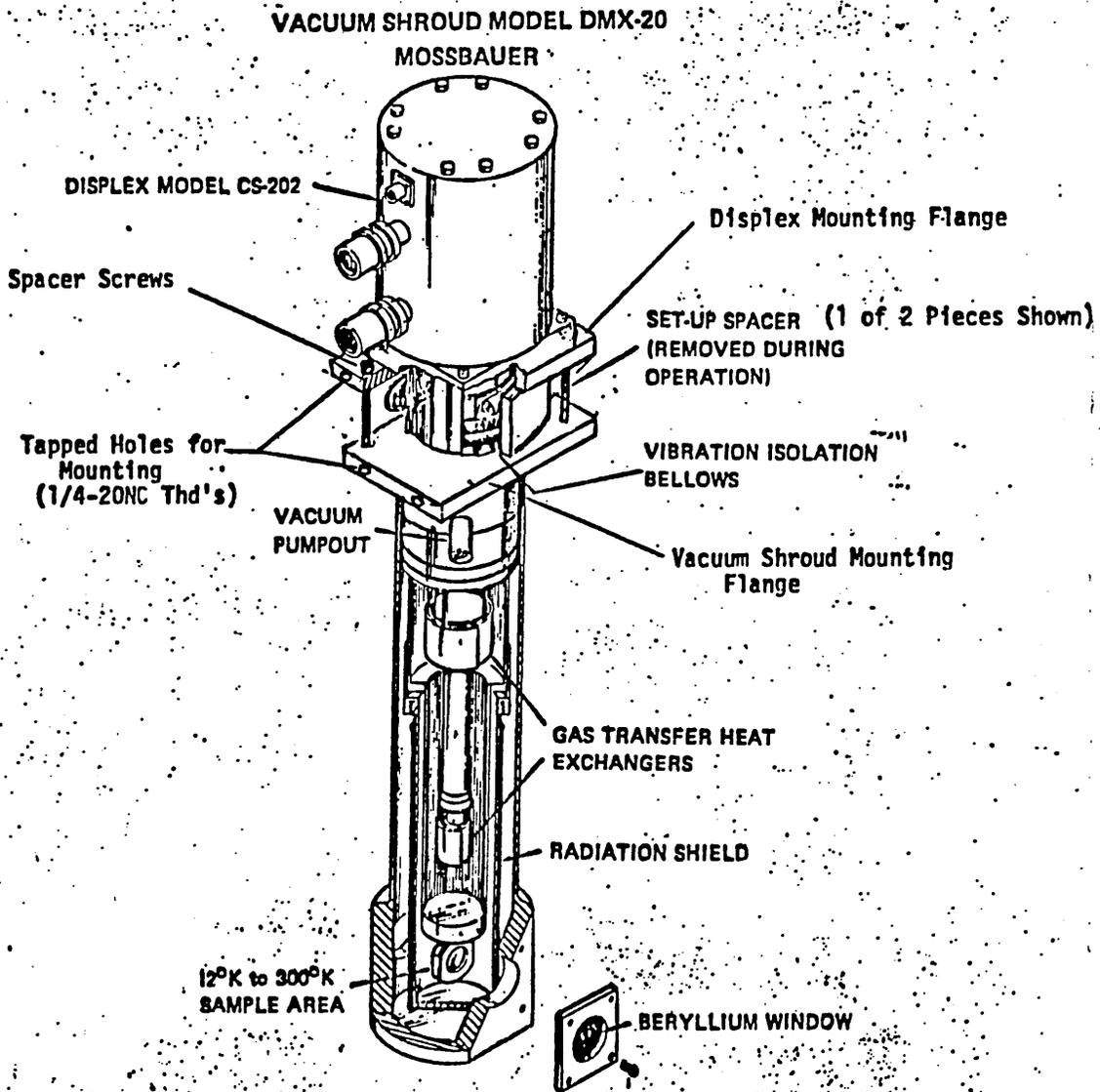
Figure 6.5 Simplified Expander Diagram

HIGH PRESSURE GAS INLET

VALVE MOTOR

ROTATING VALVE DISC

LOW PRESSURE GAS RETURN

SURGE VOLUME

ORIFICE

VALVE STEM

SLACK CAP

DISPLACER

FIRST STAGE REGENERATOR

FIRST STAGE HEAT STATION

SECOND STAGE REGENERATOR

SECOND STAGE HEAT STATION
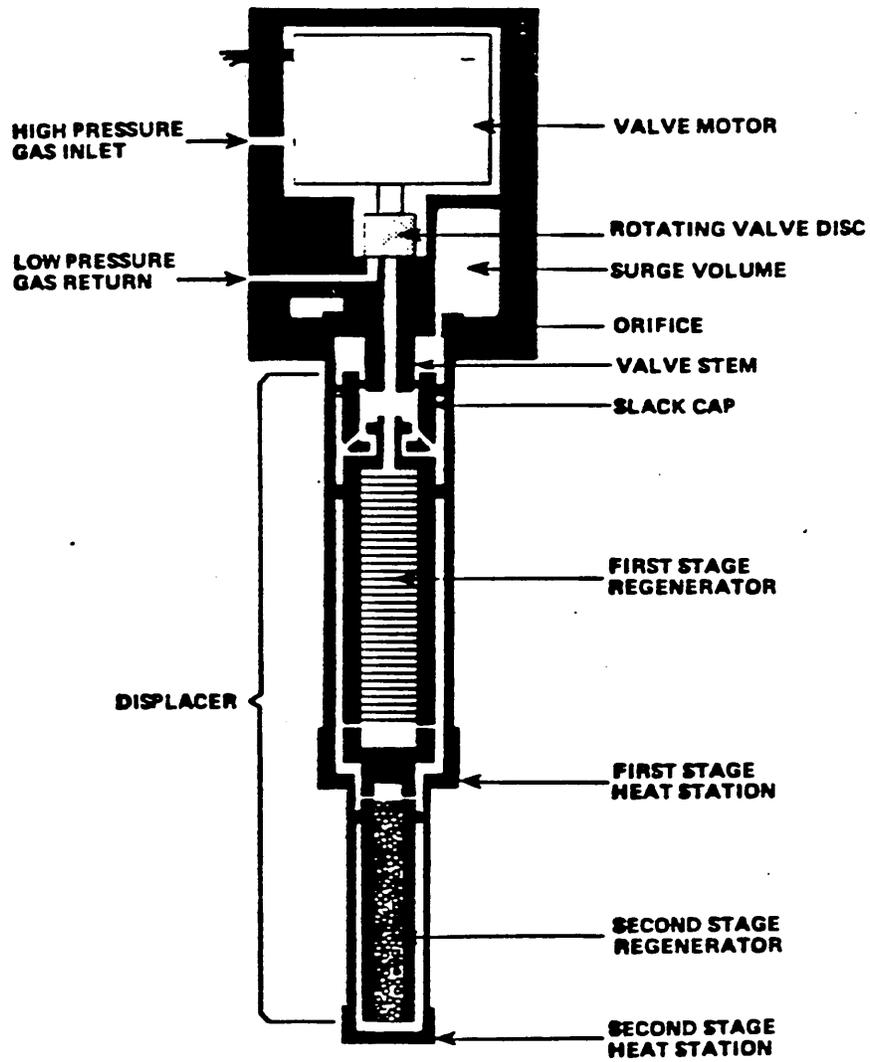
6.5 REFERENCES

1. N.N. Greenwood and T.C. Gibb, 'Mössbauer Spectroscopy' Chapman and Hall, 1971.

2. R.H. Herber and M.F. Leahy, J. Chem. Phys., 1977, 67, 2718.

3. T. Van Hoang, A. Michel and A. Guyot, Polym. Deg. and Stab., 1982, 4, 213.

4. B. Bashkirov, I. Ya Kurashin, A.S. Khramov, and A.N. Pudovik, Koord. Khim., 1980, 6, 537.

5. J.S. Brooks, R.W. Clarkson and J.M. Williams, J. Organomet. Chem., 1983, 251, 63.

CHAPTER 7 : A COMPARISON OF THERMAL AND GAMMA-IRRADIATION DEGRADATION OF ORGANOTIN-STABILISED POLY(VINYLCHLORIDE)

7.1   INTRODUCTION

7.2   RESULTS AND DISCUSSION

7.3   CONCLUSIONS

7.4   REFERENCES

7.1 INTRODUCTION

The thermal degradation of organotin-stabilised PVC is
reported to result in the blackening of the polymer[1,2]
as observed for the irradiated PVC after an exposure of
100 kGy. The discolouration associated with this severe
degradation is usually observed when stabiliser tin-
carbon bonds are cleaved.[2] Thus, the techniques used to
determine the mode of degradation of organotin stabilisers
in PVC during exposure to γ-irradiation can be similarly
applied to thermally degraded PVC in order to identify
the degradation products resulting from the stabilisation
process. A qualitative comparison between the two
degradation processes can then be made.

Samples of PVC containing dibutyltinbis(isooctylthio-
glycollate) [2] and dibutyltinbis(isooctylmaleate) [3]
were conventionally thermally degraded[3] in air at 180°C
in an oven for 120 minutes and then analysed by Mössbauer
spectroscopy and by extraction of the degradation products,
as described in Chapter 5.

7.2 RESULTS AND DISCUSSION

Figures 7.1, 7.2 and 7.3 show the Mössbauer spectra of
thermally degraded PVC containing dibutyltinbis(isooctyl-
thioglycollate) [2] in milled PVC, dibutyltinbis(isooctyl-
thioglycollate) [2] dispersed in PVC by solvent casting
(from dichloromethane) and dibutyltinbis(isooctylmaleate)
[3] in milled PVC (at 4% (w/w)) respectively. The
Mössbauer parameters recorded for the degraded PVC samples

Figure 7.1 ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC (milled) after Thermal Degradation for 120 min at 180°C recorded at 80K

ABSORPTION

VELOCITY (MM/SEC)
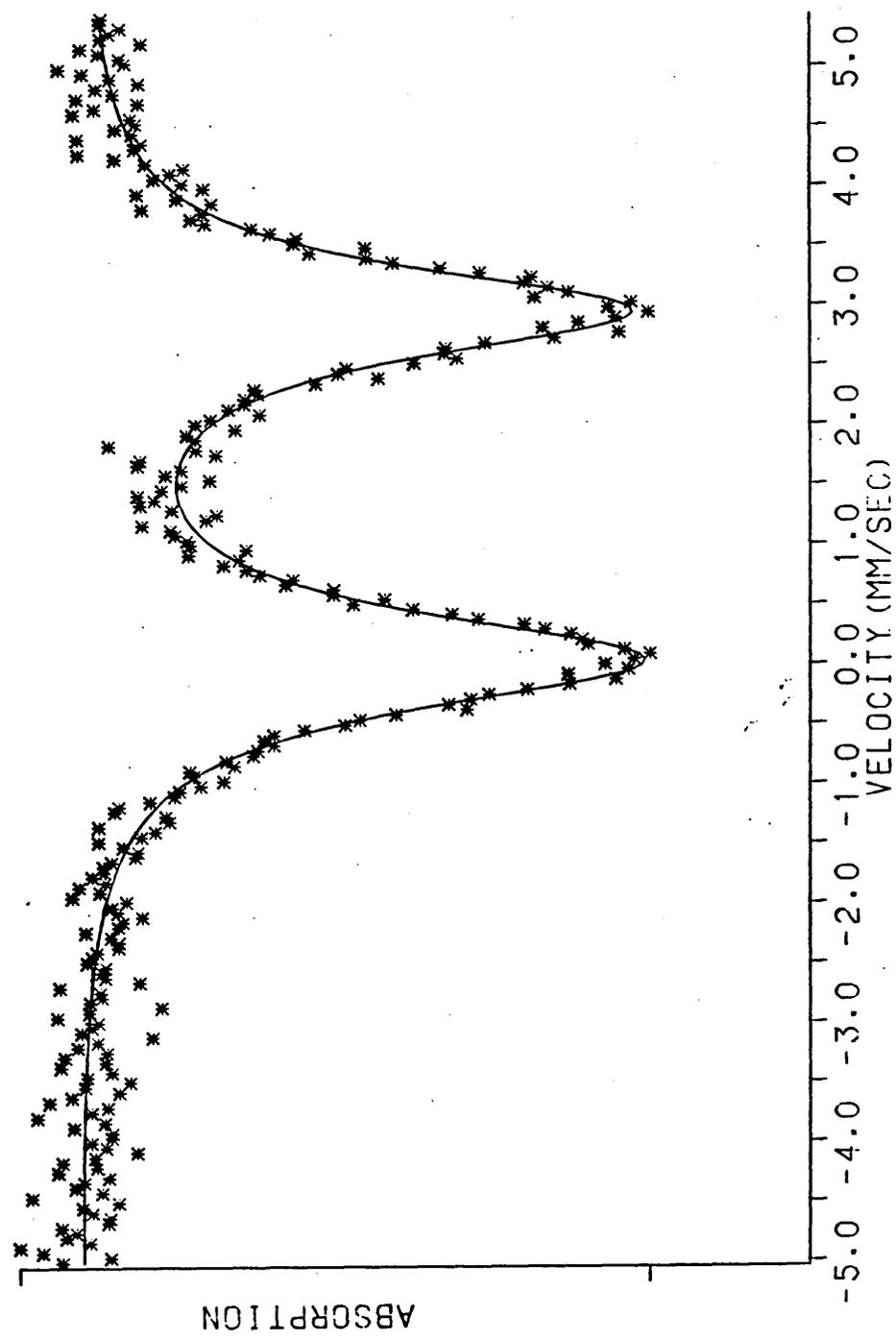
Figure 7.2 ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylthioglycollate) in PVC
(solvent cast) after Thermal Degradation for 120 min at 180°C recorded
at 80K
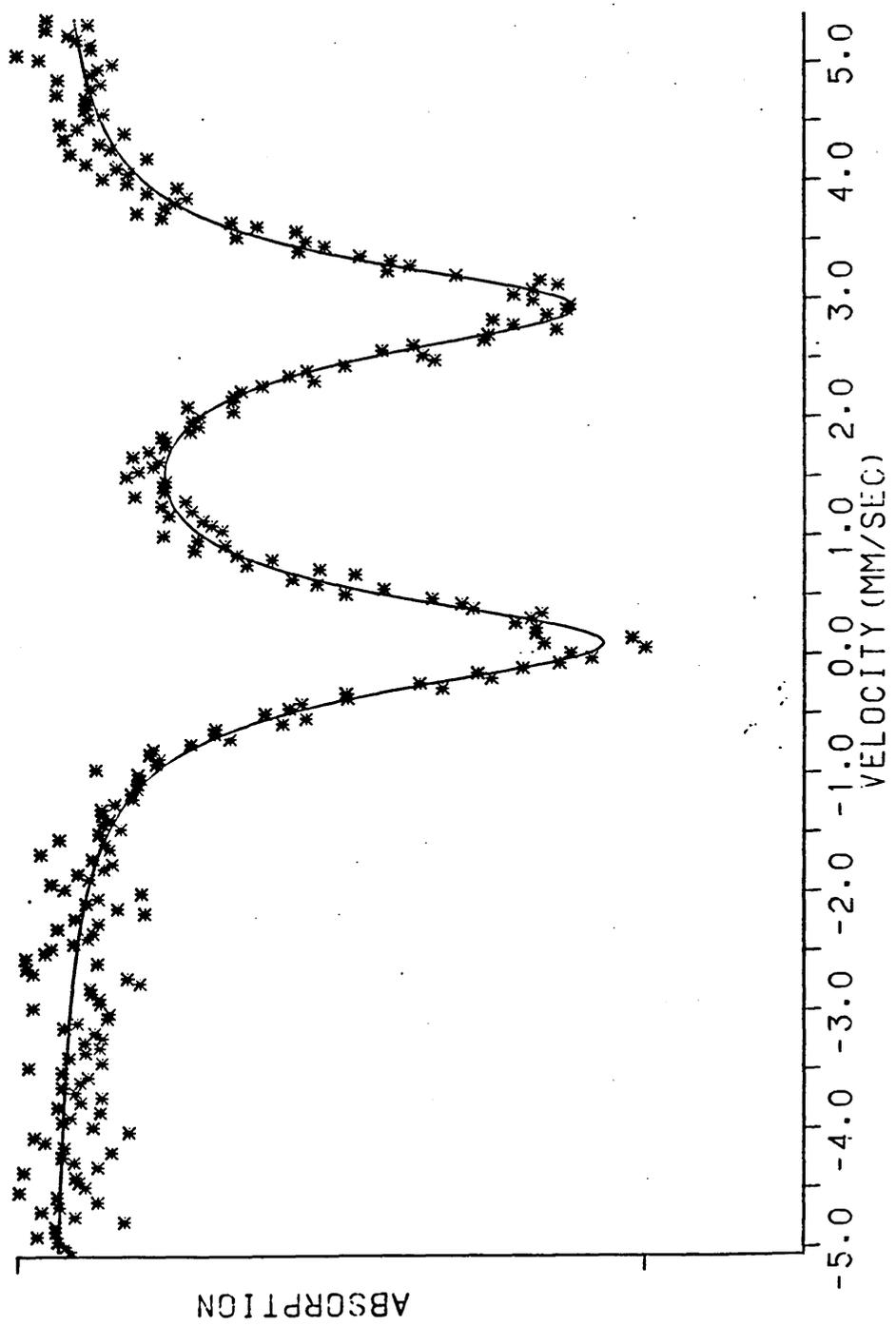
Figure 7.3 ^{119}Sn Mössbauer Spectrum of Dibutyltinbis(isooctylmaleate) in PVC (milled) after Thermal Degradation for 120 min. at 180°C recorded at 80K
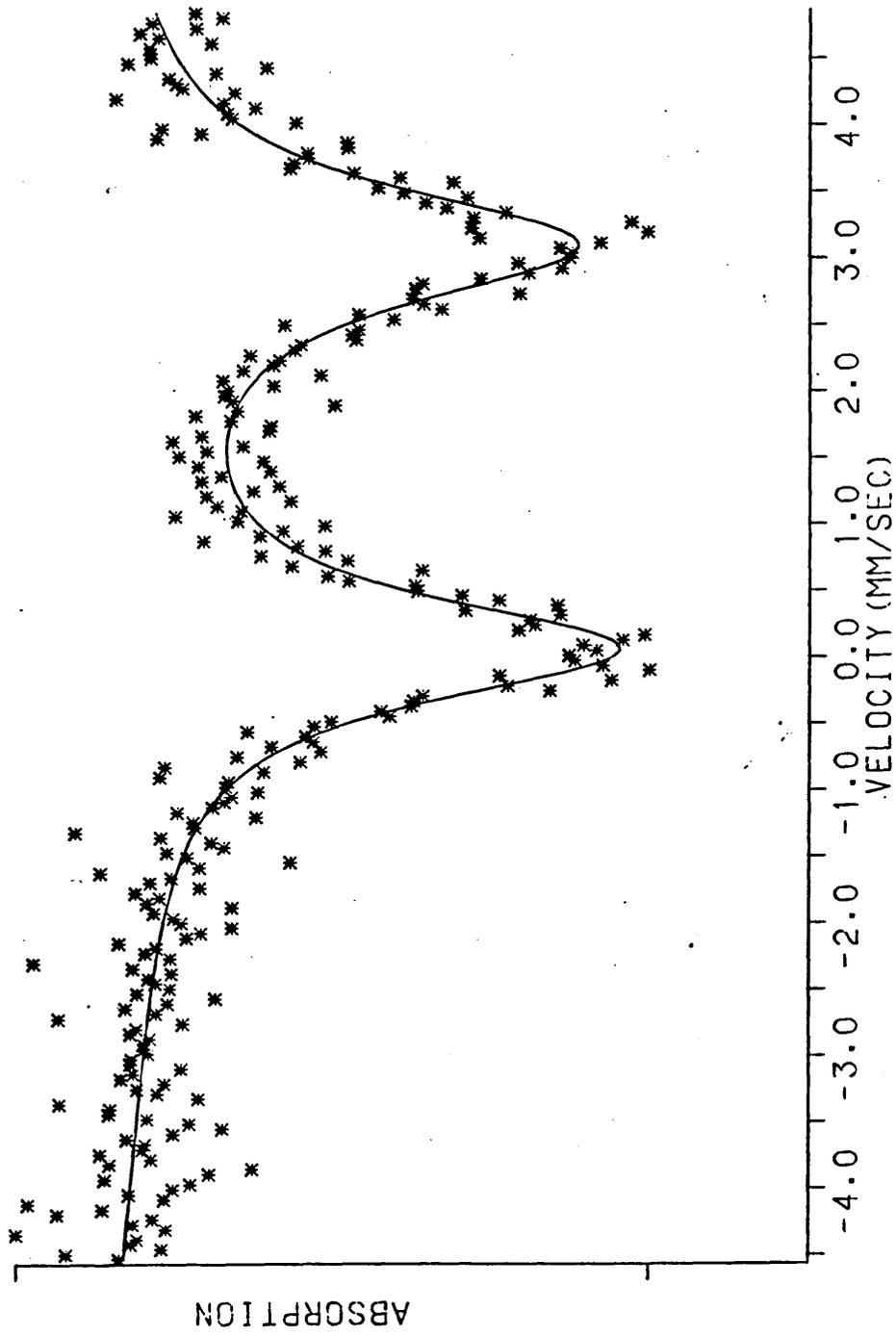
and those of degradation products in PVC, which are suggested to occur in the literature,[1,4] are given in Table 7.1.

The Mössbauer spectra show that degradation of the stabilisers [2] and [3], to components giving rise to quadrupole doublets, has occurred. For the thioglycollate stabiliser [2], it has been reported that conversion to the dibutylchlorotin thioglycollate [5] occurs.[1] However, the parameters for [5] and dibutyltin dichloride, when dispersed in PVC, ($\delta = 1.47$ mms^{-1}, $\Delta = 2.99$ mms^{-1} and $\delta = 1.50$ mms^{-1}, $\Delta = 3.02$ mms^{-1} respectively) are very similar to those observed for the thermal degradation product ($\delta = 1.46$ mms^{-1}, $\Delta = 2.93$ mms^{-1} for milled PVC and $\delta = 1.49$ mms^{-1}, $\Delta = 2.84$ mms^{-1} for solvent cast PVC) and therefore the absolute identification of the degradation product is not possible. The computer fit may also represent the sum of dibutylchlorotin thioglycollate [5] and dibutyltin dichloride components due to the similarity of their parameters when dispersed in PVC. The chromatographic results in Table 7.2 show that very little conversion to butyltin trichloride (6 and 7% respectively for milled and solvent cast samples) and stannic chloride (< 1%) has occurred. The greater part of the stabiliser [2] must have been converted to either the dibutylchlorotin thioglycollate [5] or dibutyltin dichloride or a mixture of these.

Table 7.1 ^{119}Sn Mössbauer Parameters for Thermally
Degraded PVC containing Dibutyltinbis(isooctyl-
thioglycollate) and Dibutyltinbis(isooctyl-
maleate) and Possible Degradation Products in
PVC at 80K

Sample	$\delta(mms^{-1})$	$\Delta(mms^{-1})$	$\Gamma(mms^{-1})$
4% (w/w) $Bu_2Sn(IOTG)_2$ in PVC (milled) Thermally degraded for 120 mins at 180°C	1.46	2.93	0.96
4% (w/w) $Bu_2Sn(IOTG)_2$ in PVC (solvent cast) Thermally degraded for 120 mins at 180°C	1.49	2.84	0.97
4% (w/w) $Bu_2SnCl(IOTG)$ in PVC (milled)	1.47	2.99	0.88
1.2% (w/w) Bu_2SnCl_2 in PVC (solvent cast from dichloromethane)	1.50	3.02	0.94
4% (w/w) $Bu_2Sn(IOM)_2$ in PVC (milled) Thermally degraded for 120 mins at 180°C	1.55	3.05	1.02
2% (w/w) $Bu_2SnCl(IOM)$ in PVC (solvent cast from tetrahydrofuran)	1.40	3.34	0.89

Parameters ± 0.05 mms^{-1}

Table 7.2 Chromatographic Analyses of Thermally Degraded
PVC containing Dibutyltinbis(isooctylthio-
glycollate) and dibutyltinbis(isooctylmaleate)
Thermally Degraded for 120 minutes at 180°C

Sample	Relative Concentration of tin compound (%)		
	Bu_2SnX_2	$BuSnCl_2$	$SnCl_4$
4% (w/w) $Bu_2Sn(IOTG)_2$ (milled)	94	6	< 1
4% (w/w) $Bu_2Sn(IOTG)_2$ (solvent cast)	93	7	< 1
4% (w/w) $Bu_2Sn(IOM)_2$ (milled)	92	6	2

For the maleate stabiliser [3], after thermal degradation, the Mössbauer parameters ($\delta = 1.55$ mms^{-1} and $\Delta = 3.05$ mms^{-1}) show close agreement with those of dibutyltin dichloride in PVC ($\delta = 1.50$ mms^{-1} and $\Delta = 3.02$ mms^{-1}). The major degradation product must be dibutyltin dichloride and clearly not the dibutylchlorotin maleate [6] ($\delta = 1.40$ mms^{-1} and $\Delta = 3.34$ mms^{-1}). The chromatographic analysis shows very little conversion to butyltin trichloride and stannic chloride (6 and 2% respectively).

7.3 CONCLUSIONS

The results show that extensive dealkylation of dibutyltinbis(isooctylthioglycollate) [2] and dibutyltinbis(isooctylmaleate) [3], which is observed in PVC samples blackened through γ-irradiation, does not occur during prolonged thermal degradation of such systems. The thioglycollate stabiliser [2] is converted to dibutylchlorotin thioglycollate [5] or dibutyl dichloride or a mixture of these whereas the maleate stabiliser [3] is clearly converted to dibutyltin dichloride under these conditions.

7.4 REFERENCES

1. D. W. Allen, J. S. Brooks, R. W. Clarkson,
   M. T. J. Mellor and A. G. Williamson,
   J. Organometal. Chem., 1980, 199, 199.

2. R. W. Rocket, M. Hadlington and R. W. Poyner,
   J. Appl. Polym. Sci., 1974, 18, 745.

3. G. Ayrey and R. C. Poller, in Developments in
   Polymer Stabilisation-2, Ed. G. Scott, Applied
   Science, 1980, p 7.

4. A. H. Frye, R.W. Horst and M. A. Paliohagis,
   J. Polym. Sci., 1964, A-2, 1765.

CHAPTER 8 : GENERAL CONCLUSIONS

The experimental results obtained show that the mode of
degradation of the organotin stabilisers, dioctyltinbis-
(isooctylthioglycollate) [1], dibutyltinbis(isooctyl-
thioglycollate) [2] and dibutyltinbis(isooctylmaleate) [3]
in PVC when subjected to γ-irradiation is as follows:

(i) $R_2SnY_2 \xrightarrow{\gamma, PVC} R_2SnYCl + HY$

(ii) $R_2SnYCl \xrightarrow{\gamma, PVC} R_2SnCl_2 + HY$

(iii) $R_2SnCl_2 \xrightarrow{\gamma, PVC} RSnCl_3 + RH$

(iv) $RSnCl_3 \xrightarrow{\gamma, PVC} SnCl_4 + RH$

In Chapter 3, the initial irradiation experiments showed,
from the Mössbauer spectra, that after an exposure of
100 kGy the thioglycollate stabilisers [1] and [2] are
converted to stannic chloride in milled PVC. The
maleate stabiliser [3], however, shows much less
conversion to stannic chloride and a mixture of
degradation products is clearly observed at this
exposure. The corresponding solvent cast samples for
each of the stabilisers [1], [2] and [3] show much less
degradation and this different behaviour may be attributed
to prior thermomechanical degradation of the polymer in
the milled samples which could sensitise the polymer to
γ-irradiation degradation. However, after an exposure of
200 kGy, stannic chloride is found to be the predominant
degradation product even in the solvent cast samples.

The variable dose study discussed in Chapter Four for milled PVC containing dibutyltinbis(isooctylthioglycollate) [2] shows that complex mixtures of undegraded stabiliser and degradation products are obtained at intermediate exposures up to 100 kGy. Analysis of the Mössbauer spectra at these exposures shows that, initially, rapid conversion to dibutylchlorotin thioglycollate [5] and dibutyltin dichloride has occurred at exposures up to 30 kGy, resulting from the dehydrochlorination of the polymer. The conversion to the dibutylchlorotin thioglycollate [5] is also observed in the infrared spectra of γ-irradiated PVC films.

Model irradiation studies confirm the proposed degradation pathway for the thioglycollate stabiliser [2], since each of the intermediate degradation products when dispersed in PVC is converted to stannic chloride after irradiation.

In Chapter Five, the dealkylated degradation products, butyltin trichloride and stannic chloride, have been identified for stabilisers [2] and [3] by their chromatographic separation after extraction from irradiated PVC and subsequent derivatisation. It has also been shown that for the thioglycollate stabiliser [2] a greater stabilisation effect is observed by increasing the stabiliser concentration (to 4% (w/w) which results in a retardation in colour formation at exposures up to 100 kGy, whereas at lower stabiliser concentration (1.2%

(w/w)) the polymer is completely blackened at this exposure. Much less conversion to dealkylated degradation products is also observed at exposures up to 200 kGy.

Chromatographic separation of the degradation products extracted from irradiated PVC samples containing stabilisers [2] and [3] has shown that much less conversion to stannic chloride has occurred than indicated by the Mössbauer spectra of these samples. For milled PVC containing dibutyltinbis(isooctylthioglycollate) [2] (at 1.2% (w/w)), the Mössbauer spectrum shows only one major component present which corresponds to stannic chloride. However, after derivatisation and chromato-graphic analysis, it is found that stannic chloride accounts for less than half of the tin-containing degradation products in this sample. In Chapter Six, it is shown that stannic chloride, when dispersed in PVC, has a much higher recoilless fraction than the other degradation products, at least three times larger than that determined for another degradation product, dibutyltin dichloride, in PVC. This unexpectedly large difference in recoilless fractions has been explained on the basis of the structural changes which these compounds undergo upon dispersion in PVC. This could account for the anomaly between the Mössbauer and chromatographic data. The stannic chloride component of the spectra would give rise to an intense absorption line with an absorption area approximately three times

larger than that of an equivalent concentration of dibutyltin dichloride. The stabilisers [1], [2] and [3], the dialkylchlorotin thioglycollates [4] and [5] or maleate [6], and butyltin trichloride are likely to have similarly low recoilless fractions as dibutyltin dichloride. After adjustment of the Mössbauer absorption area for stannic chloride (ie by multiplying the relative area by 1/3.1), thus compensating for the higher recoilless fraction, the Mössbauer and chromatographic data show closer agreement. Table 8.1 shows a comparison of the corrected Mössbauer absorption data and chromatographic data for the determination of stannic chloride in two organotin-stabilised PVC samples after irradiation.

The difference in magnitude of the two sets of data and the corresponding over-estimation associated with the Mössbauer technique is likely to reflect the errors associated with the computer fitting of the quadrupole doublet components of these spectra which represent the sum of the components present. There are also clear over-simplifications in the assumptions made in the Debye model in determining the recoilless fraction values for stannic chloride and dibutyltin dichloride in PVC, and the assumption that the stabilisers [2] and [3] and the remaining degradation products have identical recoilless fractions, will also contribute to the above discrepancy.

Table 8.1 Mössbauer and Chromatographic Data for the
Determination of Stannic Chloride in
Organotin-Stabilised PVC after an Exposure
of 100 kGy

Sample	Relative Concentration of Stannic Chloride (%)	
	By Mössbauer Spectroscopy	By Chromatography
$Bu_2Sn(IOTG)_2$ in PVC (solvent cast) (Table 3.2)	24	18
$Bu_2Sn(IOM)$ in PVC (milled) (Table 3.3)	55	40

Finally, the overall results show that at the likely commercial levels of irradiation ($\sim$ 10 kGy), the major degradation products of the stabilisers [1], [2] and [3] are the dialkylchlorotin thioglycollates [4] and [5] and maleate [6] together with dibutyltin dichloride, which are also the degradation products observed for the thermal degradation of PVC stabilised by these compounds (Chapter 7). Some dealkylated degradation products do occur at these levels of irradiation but most of the stabiliser degradation products ($\sim$ 90%) remain in the dialkyl-state. The organotin stabilisers studied effectively retard the dehydrochlorination of the polymer and hence discolouration at this level of irradiation. The toxicological effect of the observed tin-compounds are well known and are unlikely to present any major health hazard upon migration into foodstuffs in contact with γ-irradiated PVC packaging containing organotin stabilisers.

ACKNOWLEDGEMENTS

COURSES AND CONFERENCES ATTENDED

1. Introduction to Mössbauer Spectroscopy,
   10 x 2 hour lectures, Sheffield City Polytechnic,
   October 1982.

2. Basic Computing, 8 x 2 hour lectures, Sheffield
   City Polytechnic, October 1982.

3. The Royal Society of Chemistry Mössbauer Spectroscopy
   Discussion Group Meetings:

   (i)   University of Essex, 12-13 July 1982
   (ii) UMIST, 11-13 July 1983
   (iii) University of Oxford, 2-4 July 1984

4. Methods of Surface Analysis, One-day Short Course,
   Loughborough University of Technology,
   8 February 1984.

A ^{119m}Sn Mössbauer Study of the Degradation of Organotin Stabilised PVC by Gamma-Irradiation

John S. Brooks,* David W. Allen† & John Unwin†

* Department of Applied Physics. † Department of Chemistry.
Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, Great Britain

ABSTRACT

The technique of ^{119m}Sn Mössbauer spectroscopy has been used to study the changes which occur in three organotin stabilisers within a PVC matrix when exposed to doses of γ-irradiation up to 20 Mrad. The stabilisers studied were dioctyltinbis(iso-octylthioglycollate) [$Oct_2Sn(IOTG)_2$], dibutyltinbis(iso-octylthioglycollate) [$Bu_2Sn(IOTG)_2$] and dibutyltinbis(iso-octylmaleate) [$Bu_2Sn(IOM)_2$] incorporated into the PVC at the appropriate commercial level by conventional hot milling techniques or solvent casting. Extended doses up to 20 Mrad showed that the final degradation product for all three stabilisers is $SnCl_4$ and that the rate of degradation depends not only upon the type of stabiliser but also upon the extent of thermo-mechanical damage suffered by the PVC during processing. Mössbauer spectra were recorded at intermediate doses in the range 0·1 to 10 Mrad and yielded complex spectra containing unresolved lines corresponding to mixtures of original stabilisers and degradation products. Intermediate degradation products are proposed and rapid conversion to $SnCl_4$ is observed to start at doses greater than 3 Mrad.

INTRODUCTION

Sterilisation of food by gamma-irradiation has been known for over a decade. Radiation sterilisation requires the exposure of food, in sealed containers, to ionising radiation at absorbed doses high enough to kill all

the organisms of food spoilage. This could vary between 2·5 and 7 Mrad (25–70 kGy).[1] The absorbed radiation may also cause changes in the food and the packaging. The wholesomeness of irradiated food has been extensively investigated by many workers;[2] however, there is little published work on the packaging aspects of radiation sterilisation.[3] The most widely used polymers in food packaging are polyethylene, poly(vinyl chloride) and polystyrene. Commercial polymers, as supplied to the food packaging industry, are multi-component mixtures containing intentional and unintentional additives, e.g. antioxidants, plasticisers, stabilisers, lubricants, catalyst residues and monomers. Many of the additives will have been consumed, in part or in full, during manufacture of the polymer and converted into unknown degradation products. These polymers would then be irradiated in contact with the food under external aerobic conditions and left in contact with the food for extended periods of time. The problems posed by the possible regulation of radiation sterilisation for polymer packaged foodstuffs are therefore complex.

A survey carried out in 1962[4] on the effects of radiation on packaging materials in the dose range 1–6 Mrad concluded that, at absorbed doses of less than 1 Mrad, only minor chemical changes were induced. In 1964, the US FDA published a list of approved polymers for food contact which could be irradiated up to 1 Mrad. This list was updated in 1982 and permitted polymers, together with general classes of additives, were given.[5]

In this paper we report the findings of a systematic study of the fate of organotin stabilisers, incorporated into a PVC matrix, when exposed to doses of γ-irradiation from a cobalt-60 source. This is an extension of our previous studies of the thermal[6] and photo-chemical[7] degradation of organotin stabilised PVC. We have previously demonstrated the usefulness of [119m]Sn Mössbauer spectroscopy for the study of the changes which occur to the organotin stabiliser within the PVC matrix.

EXPERIMENTAL

Three commercially available organotin stabilisers were investigated:

(i) dioctyltinbis(*iso*-octylthioglycollate)

$(C_8H_{17})_2Sn(SCH_2COOC_8H_{17})_2$, [$Oct_2Sn(IOTG)_2$]

(ii) dibutyltinbis(*iso*-octylthioglycollate)

   $(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$, $[Bu_2Sn(IOTG)_2]$ and

(iii) dibutyltinbis(*iso*-octylmaleate)

   $(C_4H_9)_2Sn(OCOCH=CHCOOC_8H_{17})_2$, $[Bu_2Sn(IOM)_2]$.

The stabilisers were incorporated into the PVC at commercial levels, i.e. $1\cdot2\%$ w/w for the thioglycollate stabilisers and 2% w/w for maleate stabilisers, either by conventional hot milling techniques or solvent casting. Solvent casting was carried out by dissolving the PVC in the minimum amount of solvent (dichloromethane for PVC containing thioglycollate stabilisers and tetrahydrofuran for PVC containing maleate stabilisers) and allowing slow evaporation of the solvent. Sample discs (approximately $2\,cm^2$) were cut from the milled sheet or solvent cast films.

The PVC samples containing the organotin stabilisers were irradiated in air by ^{60}Co gamma-irradiation. The source used consists of ^{60}Co tubes mounted in a circular array at the bottom of a 20 ft deep water pond. The sample is loaded into watertight containers and lowered to the centre of the array, where it receives a dose rate of $0\cdot5\,Mrad/h$ at ambient temperature. Doses in the range $0\cdot1\,Mrad–20\,Mrad$ were used during the course of this investigation.

The Mössbauer spectra were recorded using a constant acceleration Mössbauer spectrometer, with a room temperature $15\,mCi$ ^{119m}Sn barium stannate source. The sample discs were cooled to $80\,K$ using a continuous flow nitrogen cryostat and helium exchange gas. The Mössbauer hyperfine parameters were obtained from computer least-squares fits to the experimental data using Lorentzian line shapes. The low levels of tin in the samples ensured 'thin' Mössbauer samples and reduced saturation effects and allowed the assumed proportionality between measured line areas and Mössbauer thickness.[8]

RESULTS AND DISCUSSION

Preliminary irradiation studies

Mössbauer spectra were recorded for each stabiliser under the conditions shown in Table 1.

TABLE 1

Mössbauer Parameters for Stabilisers in PVC at 80 K

Sample	Isomer shift[a] (mm/s) (±0·05)	Quadrupole splitting (mm/s) (±0·05)	Full width at half height (mm/s)	Relative concentration of the components present (%)
Pure $Oct_2Sn(IOTG)_2$	1·45	2·34	0·89	
$Oct_2Sn(IOTG)_2$ in PVC (Milled)	1·45	2·28	1·00	
$Oct_2Sn(IOTG)_2$ in PVC (Solvent cast)	1·43	2·43	1·16	
$Oct_2Sn(IOTG)_2$ in PVC (Milled)-irradiated (10 Mrad)	0·34		1·06	
(20 Mrad)	0·40			
$Oct_2Sn(IOTG)_2$ in PVC (Solvent cast)-irradiated (10 Mrad)	1·64	2·62	1·13	70
	0·09		0·73	30
(20 Mrad)	0·32		1·16	
Pure $Bu_2Sn(IOTG)_2$	1·46	2·29	0·89	
$Bu_2Sn(IOTG)_2$ in PVC (Milled)	1·48	2·30	0·95	
$Bu_2Sn(IOTG)_2$ in PVC (Solvent cast)	1·44	2·42	1·13	
$Bu_2Sn(IOTG)_2$ in PVC (Milled)-irradiated (10 Mrad)	0·38		1·38	
(20 Mrad)	0·41		1·02	
$Bu_2Sn(IOTG)_2$ in PVC (Solvent cast)-irradiated (10 Mrad)	1·50	2·61	1·13	70
	0·00		0·76	30
(20 Mrad)	0·36		1·02	100
Pure $Bu_2Sn(IOM)_2$	1·44	3·66	1·06	
$Bu_2Sn(IOM)_2$ in PVC (Milled)	1·40	3·38	0·88	
$Bu_2Sn(IOM)_2$ in PVC (Solvent cast)	1·36	3·34	0·98	
$Bu_2Sn(IOM)_2$ in PVC (Milled)-irradiated (10 Mrad)	1·46	2·69	1·09	30
	0·39		1·14	70
(20 Mrad)	1·40	2·50	1·08	20
	0·41		1·08	80
$Bu_2Sn(IOM)_2$ in PVC (Solvent cast)-irradiated (10 Mrad)	1·55	2·98	1·45	70
	−0·18		0·57	30
(20 Mrad)	1·40	3·48	0·86	40
	0·18		0·94	60
$Bu_2SnCl(IOM)$ in PVC (Solvent cast)-irradiated (20 Mrad)	1·59	3·18	0·92	40
	0·24		1·16	60

[a] Measured relative to $BaSnO_3$.
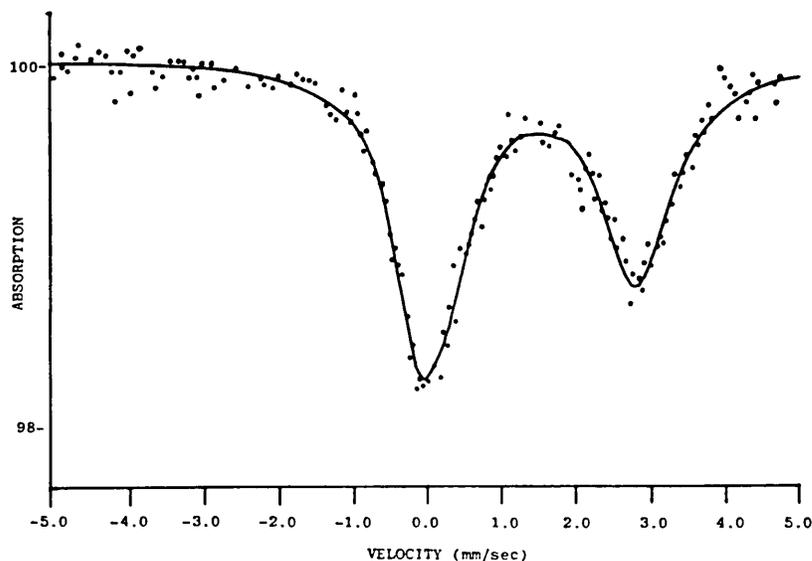
Fig. 1. Mössbauer spectrum of $Oct_2Sn(IOTG)_2$ in PVC (solvent cast) irradiated at 10 Mrad.

In all cases there was no significant structural change in the stabiliser when incorporated into the PVC; however, the response to irradiation did depend critically upon the nature of the pre-irradiation processing. For milled samples containing $Bu_2Sn(IOTG)_2$ and $Oct_2Sn(IOTG)_2$, an irradiation of 10 Mrad produced a complete conversion of the stabiliser to a final degradation product having a single line Mössbauer spectrum. For the solvent cast samples, the 10 Mrad irradiation did not produce complete conversion and a more complex Mössbauer spectrum was observed (Fig. 1). The spectra were fitted as a combination of a single line and a quadrupole doublet, although, as will be explained later, this may well be an over-simplification. Nevertheless, the computer fit indicates that approximately 30% of the stabiliser has been converted to the single line product. The maleate stabiliser, $Bu_2Sn(IOM)_2$, exhibits similar behaviour, although its rate of degradation is slower than for the thioglycollates. The milled sample, when irradiated at 10 Mrad, has only been 70% converted to the single line product while the solvent cast sample has only been 30% converted. These experiments show clearly that the stabiliser undergoes some chemical change on irradiation in a way which depends upon the processing of the polymer.

The effect of an irradiation dose of 20 Mrad is similar for

$Oct_2Sn(IOTG)_2$ and $Bu_2Sn(IOTG)_2$, in each case resulting in a single line Mössbauer spectrum corresponding to the final degradation product. Further prolonged exposure did not result in any significant change in the Mössbauer spectra. The $Bu_2Sn(IOM)_2$ stabiliser is still not fully converted after exposure to 20 Mrad although it is apparent that the milled sample degrades more rapidly and that the final degradation product is likely to be the same as observed previously. The more rapid degradation of all the milled samples appears to be a result of thermo-mechanical damage to the PVC during the milling process producing defect sites from which elimination of HCl occurs rapidly on irradiation.

Identification of the final degradation product

The Mössbauer spectra resulting from the gamma irradiation of organotin-stabilised PVC revealed many similarities to those observed in our previously reported studies of uv-induced photo-chemical degradation of these materials. In this study,[7] we showed that prolonged irradiation of PVC containing dibutyltinbis-*iso*-octylthioglycollate led to the formation of a tin-containing degradation product which exhibited a broad Mössbauer line with an isomer shift of ~ 0.40 mm s^{-1} which we attributed to the unresolved quadrupole doublet derived from stannic oxychloride, $SnOCl_2$, due to the close similarity of the observed Mössbauer parameters with those reported in the literature for the pure compound.[9] Thus it seemed possible that this compound was also being formed as the ultimate degradation product of organotin stabilisers in γ-irradiated PVC. In order to investigate this more fully, stannic oxychloride, prepared by reaction of ozonised oxygen with stannic chloride,[10] has been incorporated into PVC by solvent casting. The Mössbauer parameters for this material are presented in Table 2, together with the results of gamma-irradiation of the polymer to a dose of 10 Mrad. It is noteworthy that, upon dispersion of $SnOCl_2$ in PVC at low concentrations, the line width reduces and the isomer shift changes from 0.32 mm s^{-1} for the pure compound to 0.17 mm s^{-1} when dispersed. Upon gamma-irradiation, the isomer shift increases again to 0.33 mm s^{-1}. It seems, therefore, that stannic oxychloride is *not* the final degradation product of γ-irradiated organotin stabilised PVC, since it, too, appears to undergo conversion when exposed to an irradiation dose of 10 Mrad. Additionally, in view of the change in isomer shift observed on dispersion of $SnOCl_2$ in PVC, it would seem that it is also unlikely that this

TABLE 2

Mössbauer Parameters for Stannic Oxychloride ($SnOCl_2$) and Stannic Chloride ($SnCl_4$)

Sample	_Isomer shift_[a] _(δ/mm s^{-1}) (± 0.05)_	_Quadrupole splitting (Δ/mm s^{-1}) (± 0.05)_	_Full width at half height (Γ/mm s^{-1}) (± 0.05)_
Pure $SnOCl_2$ (Prepared)	0·32	0·72	0·98
$SnOCl_2$[b]	0·25	0·72	1·12
$SnOCl_2$ in PVC (Solvent cast) at 1 % w/w	0·17	—	1·04
$SnOCl_2$ in PVC (Solvent cast) at 1 % w/w. Irradiated at 10 Mrad	0·33	—	1·04
$SnCl_4$[c]	0·82	—	1·04
$SnCl_4$ in PVC (Solvent cast) at 1·2 % w/w	0·30	—	1·29

[a] Measured relative to $BaSnO_3$.

[b] Reference 9.

[c] Reference 11.

compound is responsible for the observed Mössbauer spectrum of uv degraded systems. (It is becoming apparent that dispersion of pure tin-containing compounds in 'inert' matrices can often lead to significant changes in Mössbauer parameters. Thus, for example, we have shown that, on dispersion of dibutyltin dichloride in PVC, the isomer shift and quadrupole splitting parameters change significantly from those of the pure substance, consistent with a breakdown of co-ordination polymer involving octahedrally co-ordinated tin atoms with the formation of dimeric units involving five-co-ordinate tin.[14])

In studies[12] using model compounds for PVC, a number of organotin stabilisers of the type R_nSnY_{4-n} (where R = alkyl or aryl; Y = alkylthio, arylthio or carbo thiolate) have been treated with hydrogen chloride at 180 °C and investigated as potential thermal stabilisers for PVC. Cleavage of tin–carbon bonds by hydrogen chloride was demonstrated, and the formation of monoalkyl (aryl) tin trichlorides or stannic chloride was shown. Stannic chloride is clearly a possible final degradation product in our studies but the isomer shift for the pure compound (0·82 mm s^{-1}) is not in agreement with the observed line position (~ 0.34 mm s^{-1}) of the degradation product. However, when $SnCl_4$ is dispersed in PVC, the isomer shift drops from 0·82 mm s^{-1} to 0·30 mm s^{-1} (Table 2). This is consistent with the Mössbauer data for the degradation product observed

in both the gamma- and uv-irradiation studies. However, the absorption line is broadened slightly upon dispersion in PVC and this may be due to different environments surrounding the $SnCl_4$ molecules, i.e. complex formation with HCl or co-ordination involving chlorine atoms of the polymer. The decrease in isomer shift for $SnCl_4$ when dispersed in PVC is consistent with similar observations by other workers[13] where a decrease is observed on complexation with hydrogen halides under non-aqueous conditions.

Thus we conclude that the final degradation product for all three stabilisers is $SnCl_4$ and that the rate of degradation depends not only upon the type of stabiliser but also the extent of thermo-mechanical damage to the PVC during processing.

Model studies of proposed degradation intermediates

It is likely that, during irradiation of PVC stabilised by an organotin compound, a sequence of reactions of the following type occurs.
For example, for $Bu_2Sn(IOTG)_2$:

$$Bu_2Sn(IOTG)_2 + HCl \rightleftharpoons Bu_2SnCl(IOTG) + H(IOTG) \tag{1}$$

$$Bu_2SnCl(IOTG) + HCl \rightleftharpoons Bu_2SnCl_2 + H(IOTG) \tag{2}$$

$$Bu_2SnCl_2 + HCl \rightarrow BuSnCl_3 + HBu \tag{3}$$

$$BuSnCl_3 + HCl \rightarrow SnCl_4 + HBu \tag{4}$$
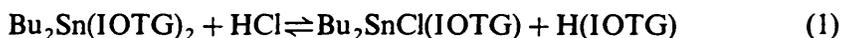
A number of other reactions are also possible:

$$Bu_2Sn(IOTG)_2 + Bu_2SnCl_2 \rightleftharpoons 2Bu_2SnCl(IOTG) \tag{5}$$

$$Bu_2SnCl_2 + SnCl_4 \rightleftharpoons 2BuSnCl_3 \tag{6}$$

Inevitably, the final product of the above reactions will be $SnCl_4$, since complex formation with hydrogen chloride will inhibit reactions of type (6). At lower absorbed doses, however, the intermediate species will doubtless be present in varying proportions. The proposed intermediate degradation products of $Bu_2Sn(IOTG)_2$ were incorporated into PVC by solvent casting, under a nitrogen atmosphere due to their moisture sensitivity. The samples were then irradiated to a dose of 20 Mrad, which corresponded to the dose required to ensure complete degradation of the original stabiliser. Mössbauer parameters are shown in Table 3. Significant changes in parameters are observed when Bu_2SnCl_2, $BuSnCl_3$ and $SnCl_4$ are incorporated into PVC by solvent casting. The reduction in

TABLE 3

Mössbauer Parameters of Degradation Intermediates in Their Pure States, when Incorporated into PVC and after Irradiation (20 Mrad)

Sample	Isomer shift[a] $(\delta/mm\,s^{-1})$ $(\pm0\cdot05)$	Quadrupole splitting $(\Delta/mm\,s^{-1})$ $(\pm0\cdot05)$	Line width $(\Gamma/mm\,s^{-1})$ $(\pm0\cdot05)$
$Bu_2Sn(IOTG)_2$ (Pure)	1·46	2·29	0·89
1·2% $Bu_2Sn(IOTG)_2$ in PVC (Milled)	1·48	2·30	0·95
after 20 Mrad	0·36		1·02
$Bu_2SnCl(IOTG)$ (Pure)	1·43	2·95	0·94
1·2% $Bn_2SnCl(IOTG)$ in PVC (Milled)	1·43	2·98	0·92
after 20 Mrad	0·31		1·02
Bu_2SnCl_2 (Pure)	1·64	3·47	0·97
1·2% Bu_2SnCl_2 in PVC (Solvent cast)	1·50	3·02	0·94
after 20 Mrad	0·36		1·04
$BuSnCl_3$ (Pure)	1·30	1·91	1·03
1·2% $BuSnCl_3$ in PVC (Solvent cast)	1·17	1·94	1·00
after 20 Mrad	0·39		1·01
Pure $SnCl_4$	0·82		·
1·2% $SnCl_4$ in PVC (Solvent cast)	0·30		1·24
after 20 Mrad	0·39		1·06

[a] Measured relative to $BaSnO_3$.

quadrupole splitting when Bu_2SnCl_2 is dispersed in PVC has been reported previously[14] and this has been attributed to the breakdown of an associated six-co-ordinate structure and the formation of dimeric units involving five-co-ordinate tin. The large change in the isomer shift observed for the singlet of $SnCl_4$ when incorporated into PVC seems likely to be the result of co-ordination of Cl atoms of the PVC to the tin, resulting in a tetrahedral to pseudo-octahedral transformation.

Table 3 also shows that, after irradiation at 20 Mrad in each case, the tin compound has degraded to a singlet having an isomer shift in the range $0\cdot31$–$0\cdot39\,mm\,s^{-1}$. It is interesting to note the change in isomer shift of $SnCl_4$ in PVC from $0\cdot30$ to $0\cdot39\,mm\,s^{-1}$ after irradiation. This indicates that the degrading polymer has interacted with $SnCl_4$, probably by the formation of a complex with HCl liberated from the polymer. Similar isomer shifts have been reported for $SnCl_4$–HCl complexes in solution in liquid hydrogen halides.[13] It therefore appears that each of the possible degradation intermediates, when exposed to 20 Mrad, has

degraded to a singlet having an isomer shift between that observed for PVC containing $SnCl_4$ and irradiated PVC containing $SnCl_4$.

Variable dose studies of $Bu_2Sn(IOTG)_2$ in PVC

Samples of PVC containing $1\cdot2\%\,Bu_2Sn(IOTG)_2$, incorporated by hot milling, were subjected to a range of doses between $0\cdot1$ and $10\,$Mrad. The computer fits to the Mössbauer spectra are shown in Fig. 2. At intermediate dose levels, the complex spectra contain unresolved lines corresponding to mixtures of original stabiliser and degradation products. The solid line represents a computer fit using two lines of variable position, width and depth. This is not intended to reflect the actual nature of the spectra which will contain many components arising from the various products present, but merely serves to illustrate some interesting points. The Mössbauer parameters, and the line positions for the possible degradation products, are shown in Table 4. The overlap of lines corresponding to the original stabiliser ($Bu_2Sn(IOTG)_2$), the monochloroester ($Bu_2SnCl(IOTG)$) and dibutyltindichloride (Bu_2SnCl_2) would make it impossible to uniquely identify these components if present in varying composition depending upon dose level. The fitted data have been analysed in terms of the individual doublet line positions as shown in Table 5. Several interesting points are revealed by these data which may indicate the degradation route and the rate of degradation. The position

TABLE 4

The Mössbauer Parameters for the Possible Degradation Products of $Bu_2Sn(IOTG)_2$ in PVC after Irradiation

Sample	Line positions ($mm\,s^{-1}$) Line 1	Line 2	Isomer shift[a] ($\delta/mm\,s^{-1}$) ($\pm0\cdot05$)	Quadrupole splitting ($\Delta/mm\,s^{-1}$) ($\pm0\cdot05$)	Line width ($\Gamma/mm\,s^{-1}$) ($\pm0\cdot05$)
$1\cdot2\%$ $BuSn(IOTG)_2$ (Milled)	$0\cdot31$	$2\cdot62$	$1\cdot47$	$2\cdot31$	$0\cdot95$
$1\cdot2\%$ $Bu_2SnCl(IOTG)$ (Milled)	$-0\cdot06$	$2\cdot93$	$1\cdot44$	$2\cdot99$	$0\cdot92$
$1\cdot2\%$ Bu_2SnCl_2 (Solvent cast)	$-0\cdot02$	$3\cdot01$	$1\cdot50$	$3\cdot03$	$0\cdot94$
$1\cdot2\%$ $BuSnCl_3$ (Solvent cast)	$0\cdot20$	$2\cdot14$	$1\cdot17$	$1\cdot94$	$1\cdot00$
$1\cdot2\%$ $SnCl_4$ (Solvent cast)	$0\cdot30$		$0\cdot30$		$1\cdot24$
$1\cdot2\%$ $SnCl_4$. Irradiated at 20 Mrad	$0\cdot39$		$0\cdot39$		$1\cdot06$

[a] Measured relative to $BaSnO_3$.
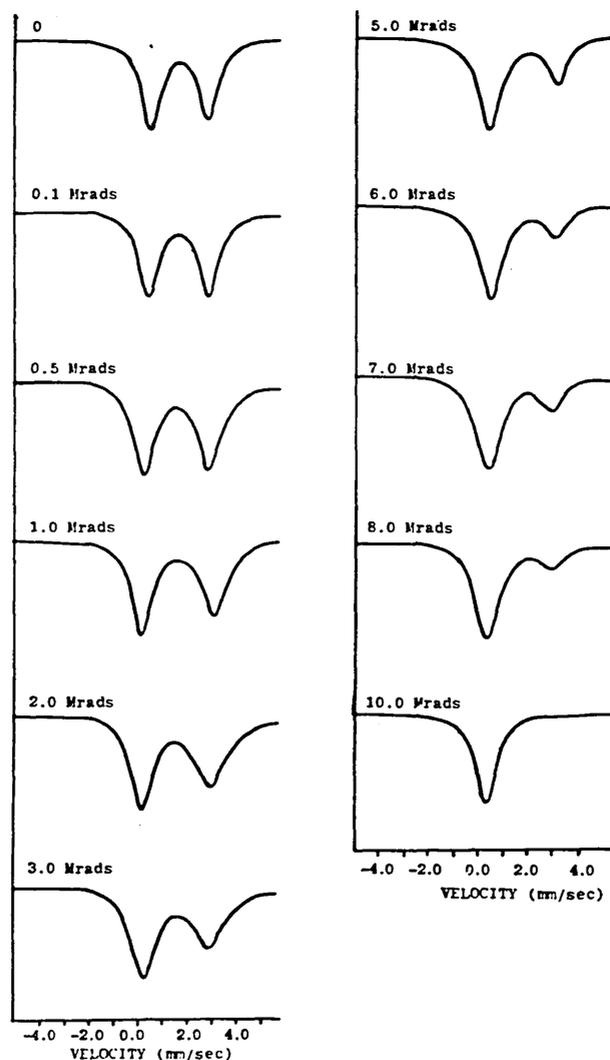
Fig. 2. Computer fits to spectra of PVC containing 1·2% $Bu_2Sn(IOTG)_2$ irradiated at doses between 0·1 and 10 Mrad.

of line 1 gradually moves to lower velocities as the dose increases to 2 Mrad indicating the conversion of the original stabiliser to the $Bu_2SnCl(IOTG)$ or Bu_2SnCl_2. This is supported by the corresponding increase in velocity of line 2. At doses above 3 Mrad, the relative intensity of line 2 starts to decrease significantly, indicating the formation of $SnCl_4$ (a singlet); also, the position of line 1 starts to increase towards the isomer

John S. Brooks, David W. Allen, John Unwin

TABLE 5

The Line Positions Observed after Irradiation of 1·2% Bu$_2$Sn(IOTG)$_2$ in PVC at Doses Between 0 and 10 Mrad

Dose (Mrad)	Line 1				Line 2				Area line 1 / Area lines 1 + 2
	Position (mm s^{-1})	Width (mm s^{-1})	Relative intensity	Relative area	Position (mm s^{-1})	Width (mm s^{-1})	Relative intensity	Relative area	
0	0·31	0·95	1·00	0·96	2·62	0·95	1·00	0·96	0·50 (5)
0·1	0·27	1·00	1·00	1·00	2·68	1·02	0·96	0·98	0·51 (5)
0·5	0·07	1·16	1·00	1·16	2·71	1·26	0·92	1·16	0·50 (5)
1·0	0·04	1·00	1·00	0·99	2·93	1·34	0·82	1·10	0·47 (5)
2·0	0·07	1·12	1·00	1·12	2·81	1·74	0·78	1·34	0·46 (5)
3·0	0·17	1·26	1·00	1·26	2·81	1·78	0·67	1·19	0·51 (5)
5·0	0·24	1·14	1·00	1·14	2·97	0·96	0·45	0·43	0·73 (5)
6·0	0·28	1·22	1·00	1·22	2·88	1·58	0·31	0·49	0·81 (5)
7·0	0·28	1·40	1·00	1·42	2·81	1·16	0·34	0·39	0·78 (5)
8·0	0·29	1·28	1·00	1·28	2·92	1·28	0·24	0·31	0·81 (5)
10·0	0·34	1·02	1·00	1·02					1·00 (5)

Fig. 3.   Plot of line areas as a function of irradiation dose.

shift corresponding to that of $SnCl_4$. However, there is no strong evidence for the formation of $BuSnCl_3$ which should produce an absorption line at $2\cdot14\,mm\,s^{-1}$.

Figure 3 shows the variation of the normalised area of line 1 as a function of absorbed dose. There is no significant change up to 3 Mrad, whereupon the formation of $SnCl_4$ is then rapid up to complete conversion at 10 Mrad. Figure 4 shows the optical density of the
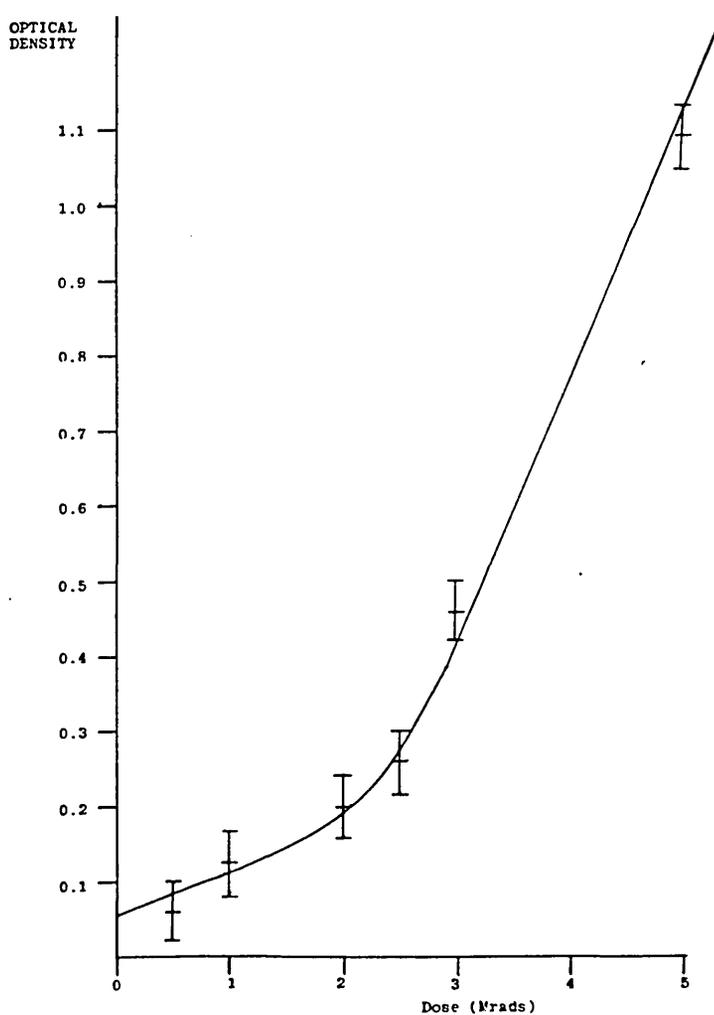
Fig. 4. Optical density of PVC containing $1\cdot2\%$ $Bu_2Sn(IOTG)_2$ as a function of irradiation dose.

irradiated PVC discs measured using a micro-densitometer. The optical density, measured in arbitrary units, remains approximately constant up to 3 Mrad and then rapidly increases, corresponding to the formation of $SnCl_4$.

Infra-red studies of irradiated PVC films containing 1·2 % $Bu_2Sn(IOTG)_2$

Bellenger *et al.*[15] have shown that infra-red spectroscopy can be used to estimate quantitatively the conversion of $Bu_2Sn(IOTG)_2$ to $Bu_2SnCl(IOTG)$ after thermal degradation of PVC containing $Bu_2Sn(IOTG)_2$. The absorbance of $Bu_2SnCl(IOTG)$ was measured at $1670 cm^{-1}$, which corresponds to the absorption by the intramolecular co-ordinated carbonyl of the thioglycollate group attached to the tin. The absorption due to the carbonyls of $Bu_2Sn(IOTG)_2$ was observed at $1730 cm^{-1}$.

Thin films of PVC containing 1·2 % $Bu_2Sn(IOTG)_2$ were prepared by solvent casting. No shift of the carbonyl absorption was observed for $Bu_2Sn(IOTG)_2$ when incorporated into PVC. (This was also the case when $Bu_2SnCl(IOTG)$ was incorporated into PVC.)

The PVC film containing 1·2 % $Bu_2Sn(IOTG)_2$ after irradiation at 10 Mrad showed a further absorption band at $1670 cm^{-1}$ which indicates some conversion of the $Bu_2Sn(IOTG)_2$ to $Bu_2SnCl(IOTG)$.

After irradiation of similar films to 20 Mrad, carbonyl absorption due to $Bu_2SnCl(IOTG)$ was absent from the infra-red spectra, consistent with its conversion to $SnCl_4$, as indicated by the Mössbauer results.

CONCLUSIONS

The three stabilisers studied were shown to degrade to the same degradation product at doses of 20 Mrad and, on the basis of model studies, this has been identified as $SnCl_4$. The rate of degradation—and subsequent formation of $SnCl_4$—has been shown to depend not only upon the type of stabiliser but also upon the extent of thermo-mechanical damage incurred by the PVC during processing. Under conventional hot milling preparation, the maleate $Bu_2Sn(IOM)_2$ has been shown to be the most stable of the three stabilisers studied, up to doses of 10 Mrad. At intermediate doses in the range 0·1 to 10 Mrad, the Mössbauer spectra consist of several overlapping lines corresponding to mixtures of the

original stabiliser and degradation products. In the case of the $Bu_2Sn(IOTG)_2$ stabiliser, which was studied in some detail, evidence was found for the existence of $Bu_2SnCl(IOTG)_2$ and Bu_2SnCl_2 as intermediate degradation products, and this has been supported by infrared studies.

ACKNOWLEDGEMENTS

REFERENCES

1. E. S. Josephson, *J. Food Safety*, **5**, 161 (1983).
2. E. S. Josephson, M. H. Thomas and W. K. Calhoun, *J. Food Proc. Preserv.*, **2**, 299 (1978).
3. G. Hoeser and A. Schwarze, *Plastics and Rubber: Materials and Applications*, 93 (August 1979).
4. G. O. Payne and C. C. Schmiege, Survey of Packaging Requirements for Radiation-Pasteurised Foods, USAEC Contract No. AT(11-1)-989, NY, USA: Cont. Can. Co. Inc. (1962).
5. US Food and Drug Administration, Code of Federal Regulations, Title 21, Chapter 1, Part 179 (1982).
6. D. W. Allen, J. S. Brooks, R. W. Clarkson, M. T. J. Mellor and A. G. Williamson, *J. Org. Met. Chem.*, **199**, 299 (1980).
7. J. S. Brooks, R. W. Clarkson, D. W. Allen, M. T. J. Mellor and A. G. Williamson, *Polym. Deg. and Stab.*, **4**, 359 (1982).
8. J. M. Williams and J. S. Brooks, *Nucl. Inst. and Methods*, **128**, 363 (1975).
9. R. H. Herber, *J. Inorg. Nucl. Chem.*, **35**, 67 (1973).
10. K. Dehnicke, *Z. anorg. allg. Chem.*, **338**, 279 (1965).
11. K. Burger, A. Vertes and I. Zay, *Inorg. Chim. Acta*, **76**, 2247 (1983).
12. B. W. Rockett, M. Hadlington and W. R. Poyner, *J. Appl. Polym. Sci.*, **18**, 745 (1974).
13. M. Katada, H. Kanno and H. Sano, *Polyhedron*, **2**. 104 (1983).
14. J. S. Brooks, R. W. Clarkson and D. W. Allen, *J. Org. Met. Chem.*, **243**, 411 (1983).
15. V. Bellenger, J. Verdu, L. B. Carette, Z. Vymalalova and Z. Vymazal, *Polym. Deg. and Stab.*, **4**, 303 (1982).

Gamma irradiation of food contact plastics: identification of tin-containing intermediates in the degradation of organotin-stabilised PVC by gamma irradiation

David W Allen,* John S Brooks,† and John Unwin*

Departments of Chemistry* and Applied Physics,†
Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB

and John D McGuinness

Food Science Division, Ministry of Agriculture, Fisheries and Food,
Great Westminster House, London SW1P 2AE

The use of ionising radiation as a process for food preservation has been under study for over 30 years. In the United Kingdom, the Food (Control of Irradiation) Regulations 1967, as amended, forbid the sale of irradiated food for human consumption, other than for patients needing sterile diets as part of their treatment.

However, the position is currently being reviewed by the Advisory Committee on Irradiated and Novel Foods in the light of the 1981 report of the Joint FAO/IAEA/WHO Expert Committee on Irradiated Food (JECFI),[1] which concluded that irradiation of any food commodity up to an overall dose of 10 kGy (1 Mrad) presents no toxicological hazard. Whereas many types of irradiated foods have been studied in depth, a survey of food packaging[2] has indicated a lack of information on the effects of gamma irradiation on plastics. It has been demonstrated that most food packaging materials perform satisfactorily at doses of 10-60 kGy and that at radiation levels of 10 kGy or less, only minor changes are induced. However, little has been reported on the effect of irradiation on the many additives present in plastics, although it has been established that changes do occur in the migration behaviour of such additives.[3]

Poly(vinyl chloride) (PVC), stabilised by organotin compounds, is widely used in the food packaging industry. Following earlier studies of the fate of organotin stabilisers present in PVC on subsequent thermal[4,5] or photochemical (artificial sunlight) degradation[6] of the polymer, using [119m]Sn Mössbauer spectroscopy, this approach has been extended to the investigation of changes undergone by such stabilisers when the polymer is subjected to varying degrees of gamma irradiation in the range 0-200 kGy (0-20 Mrads). It was shown that organotin stabilisers, e.g. dibutyltinbis-(isooctylthioglycollate) and dibutyltinbis (isooctylmaleate), undergo fairly rapid degradation with cleavage of tin-sulphur or tin-oxygen linkages and also with progressive dealkylation to form tin(IV) chloride as the major degradation product. From the Mössbauer results the extent of conversion to tin (IV) chloride appears to increase significantly after a dose of only 25 kGy (2.5 Mrads) at which point the polymer has also begun to discolour.[7] Owing to the relative insensitivity of the Mössbauer technique at the low concentrations of tin-containing compounds present in the degrading polymer, the authors have sought additional supporting chemical

Table Analysis of irradiated PVC containing organotin stabilisers

Stabiliser	Dose (kGy)	Bu_2SnX_2 (per cent)	$BuSnX_3$ (per cent)	SnX_4 (per cent)
$Bu_2Sn(SCH_2CO_2C_8H_{17})_2$	0	92	6	2
1.2 per cent w/w	5	87	10	3
	10	88	7	5
	15	75	15	10
	20	72	17	11
	25	70	16	14
	50	52	14	34
	100	35	18	47
	200	15	17	68
$Bu_2Sn(O_2C.CH=CH.CO_2C_8H_{17})_2$	0	97	3	< 1
2 per cent w/w	5	91	5	4
	10	90	7	3
	15	92	4	4
	20	92	4	4
	25	89	6	5
	50	68	16	16
	100	59	22	19
	200	41	17	42

and spectroscopic evidence of the course of degradation and now present a brief account of the findings.

On the basis of these studies, it is reasonable to assume that the following progressive degradation sequence is involved:

$$Bu_3SnY_2 \xrightarrow[HCl]{?} Bu_2SnClY \xrightarrow[HCl]{?} Bu_2SnCl_2 \xrightarrow[HCl]{?} BuSnCl_3 \xrightarrow[HCl]{?} SnCl_4$$

(Y = $SCH_2CO_2C_8H_{17}$ or $O_2C.CH=CH.CO_2C_8H_{17}$)
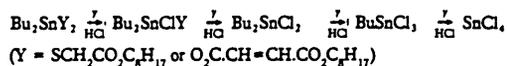
In the case of the thioglycollate stabiliser, the formation of the monochloro ester $Bu_2SnCl(SCH_2CO_2C_8H_{17})$ in the early stages of irradiation is revealed by infrared spectroscopy. Whereas the parent stabiliser exhibits a carbonyl stretching band at 1720 cm^{-1}, the monochloro ester gives rise to an absorption band at 1670 cm^{-1} due to intramolecular coordination of the carbonyl group to tin.[8,9] After an irradiation dose of 1 kGy (0.1 Mrad), the 1670 cm^{-1} absorption is observed as a shoulder on the main carbonyl band at 1720 cm^{-1}, but intensifies steadily as irradiation proceeds until after a dose of 5 kGy (0.5 Mrad) it is observed as a well-resolved absorption band. This band is still present (though at reduced intensity) in samples which have received extended irradiation of 100 kGy (10 Mrad). Earlier Mössbauer studies[7] are also consistent with the formation of the monochloro ester.

For the analysis of a potential mixture of dibutyltin compounds, butyltin trichloride and tin(IV) chloride, the procedure adopted was to dissolve the irradiated polymer in tetrahydrofuran and to treat the resulting solution with an excess of *n*-propylmagnesium chloride, thereby converting the above into a mixture of dibutyldipropyl-, butyltripropyl- and tetrapropyl- stannanes, which after removal of the polymer by precipitation with methanol, could be analysed by gas chromatography (10' column of SE30 on celite, at 200°C). Control experiments indicated the absence of redistribution reactions between the halotin compounds under the conditions used. This approach was applied to PVC samples stabilised by dibutyltinbis-(isooctylthioglycollate) (1.2 per cent w/w) and dibutyltinbis-(isooctylmaleate) (2.0 per cent w/w), respectively, which had been prepared by hot milling. The analytical results are presented in the Table.

The results indicate clearly the presence of varying amounts of monobutyltin intermediates, and a steady increase in the amount of tin(IV) chloride as the irradiation progresses. Application of this approach to similar milled samples of PVC, which had been thermally degraded for 120 min at 180°C, revealed only a trace of tin(IV) chloride and *ca* 5 per cent of monobutyltin species, most of the tin still being present in the dibutyl state. Such thermally degraded films had also undergone extensive blackening, as also had films subjected to a relatively large irradiation (e.g. 100 kGy). However, the extent of degradation of the stabiliser on prolonged gamma irradiation is much more severe than in thermal degradation. This finding is particularly significant given the greater propensity of degradation products of organotin stabilisers to migrate into food than the stablisers themselves.[10,11] Therefore, it is perhaps reassuring to note that at an irradiation level of 10 kGy the degradation process is not far advanced, and little physical change in the appearance of the polymer is apparent.

References

1 Report of a Joint FAO/IAEA/WHO Expert Committee, W.H.O. Technical Report Series, 1981, No. 659
2 Elias, P.S., *Chem. Ind. (London)*, 1979, 336-41
3 Figge, K., & Freytag, W., *Deutsche Lebensmittel-Rundschau*, 1977, **73** 205-10
4 Allen, D.W., Brooks, J.S., Clarkson, R.W., Mellor, M.T.J., and Williamson, A.G., *Chem. Ind. (London)*, 1979, 663-4
5 *Idem, J. Organomet. Chem.*, 1980, **199**, 299-310
6 Brooks, J.S., Clarkson, R.W., Allen, D.W., Mellor, M.T.J., & Williamson, A.G., *Polym. Deg. and Stab.*, 1982, **4** 359-63
7 Brooks, J.S., Allen, D.W., & Unwin, J., *ibid*, 1985, **10**, 79-94
8 Bellenger, V., Verdu, J., Carette, L.B., Vymalalova Z., & Vymazal, Z., *ibid*, 1982, **4**, 303-12
9 Cooray, B.B., *ibid*, 1984, **7**, 1-12
10 Figge, K., & Zeman, A., *Kunststoffe*, 1973, **63**, 543-50
11 Haesen, G., Depaus, R., Van Tilbeurgh, H., Le Goff, B., & Lox, F., *Journal of Industrial Irradiation Technology*, 1983, **1**, 259-80