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Synthesis, storage, and transfer of [^{210}Pb]-$(CH_3)_3PbCl$ across tomato fruit cuticle

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An improved synthetic route to [^{210}Pb]-$(CH_3)_3PbCl$ is described in which chelated $^{210}Pb^{2+}$ is methylated to [^{210}Pb]-$(CH_3)_4Pb$ with methylmagnesium bromide (CH_3MgBr) in the presence of methyl iodide. Controlled oxidation of the product with anhydrous hydrochloric acid and purification of the crude product by reversed-phase high-pressure liquid chromotography (HPLC) resulted in [^{210}Pb]-$(CH_3)_3PbCl$ in 71% radiochemical yield. Whereas storage of the purified product at −10 °C resulted in complete conversion to Pb^{2+} during one year, storage in 20% acetic acid at 4 °C resulted in less than 15% decomposition during six months. Periodic complexometric extractions to remove ^{210}Pb radioactive daughters (^{210}Bi, 100% β, E_{max} = 1.16 MeV; ^{210}Po, 100% α, E = 5.305 MeV) from the storage solution did not alter the rate of decomposition. The rate of translocation of [^{210}Pb]-$(CH_3)_3Pb^+$ across an isolated tomato cuticle was approximately twice the rate of transfer of inorganic lead(II) and was not influenced by the presence of increasing amounts of disodium ethylenediaminetetra-acetate.

Keywords: Lead-210, organolead, synthesis, migration, plant tissue, analysis

INTRODUCTION

The relative persistence and transformation rates of ionic alkylleads in different environmental compartments have not been studied in detail. In particular, the rates of mineralization of organolead species, when present at environmentally relevant concentrations in biological matrices, are lacking. The estimation of these rates is especially difficult because the total concentrations of inorganic lead(II) in virtually all biological matrices is several orders of magnitude greater than the quantities which may result from the degradation of aklylleads. When coupled with suitable chromatographic procedures and counting techniques the use of radiolabelled substrates does provide a sensitive experimental probe for the quantitation of individual lead-containing species and is ideally suited to the determination of transformation rates in biological matrices.

Lead-210 (^{210}Pb) is a naturally occurring radionuclide [predominantly β-decay, half-life ($t_{1/2}$) = 22.0 years] from the uranium-238 series which decays to the stable isotope lead-206 (^{206}Pb) via two radioactive daughter isotopes, bismuth-210 (β-decay, $t_{1/2}$ = 5.01 days) and polonium-210 (α-decay, $t_{1/2}$ = 138.4 days). The commercial availability of $^{210}Pb^{2+}$ of high specific activity and its relatively long half-life make ^{210}Pb the nuclide of choice for labelling studies. On the other hand, the short half-lives of the daughters (relative to ^{210}Pb) result in the slow development of a steady state called secular equilibrium[1] (^{210}Bi, 51 days; ^{210}Po, 2 years) which complicates counting procedures for mixtures where this equilibrium condition has not been reached. Counting algorithms to correct for variable amounts of quench and non-secular equilibrium conditions have been developed recently for ^{210}Pb quantitation by liquid scintillation counting.[2]

Electrochemical routes to [^{14}C]-$(CH_3)_3PbCl$ and [^{210}Pb]-$(CH_3)_3PbCl$,[3,4] which resulted in products with the high specific activities required for environmental and biological studies, were reported. Of the two routes, the electrochemical labelling with ^{210}Pb was the more complex. The 3 mol dm^{-3} nitric acid solution (which contained the $^{210}Pb^{2+}$) had to be

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evaporated to dryness and replaced by 0.3 mol dm^{-3} nitric acid before the labelled substrate could be reproducibly electrodeposited on copper cathodes. The copper supports, coated with the elemental nuclide, were then transferred to a two-compartment reactor, in which the ^{210}lead(0) ($^{210}Pb^0$) was electrochemically oxidized to [^{210}Pb]-$(CH_3)_4Pb$ [in dimethylformamide containing an inert electrolyte sodium perchlorate ($NaClO_4$) and a methyl group donor iodomethane (CH_3I)]. The labelled organometallic product was oxidized to [^{210}Pb]-$(CH_3)_3PbCl$ with hydrogen chloride (HCl) gas, purified by thin-layer chromatography, and stored, as an aqueous solution, at −20 °C. Although the preparation of [^{210}Pb]-$(CH_3)_4Pb$ and the thin-layer chromatographic purification of the final product were relatively efficient, they were both time-consuming and somewhat hazardous since ^{210}Pb and daughters are removed from solution during these steps. Because of their long-range energetic emissions in air, ^{210}Pb (γ, E_{ave} = 46.52 MeV) and its first daughters ^{210}Bi β, E_{max} = 1.16 MeV) are best handled in dilute solutions where their energetic radiations are efficiently absorbed. The oxidation step had also been difficult to control. Finally, because of the decay of ^{210}Pb, the organometallic product is predicted to be continuously bombarded by relativistic electrons (from ^{210}Bi decay) and α-particles (from ^{210}Po decay). This phenomenon may induce radiolysis of the product upon long-term storage and may have accounted for the degradation to Pb^{2+} which was virtually complete over one year. The objectives of the present study were to improve methods for the synthesis, purification and storage of [^{210}Pb]-$(CH_3)_3PbCl$. In addition, preliminary experiments were to be conducted to determine the relative rates of transfer of $(CH_3)_3Pb^+$ and of Pb^{2+} across plant cuticles.

The cuticular membrane, a non-cellular structure which covers the epidermal layers of fruits, stems, and leaves of higher plants, plays an important protective role as a selectively permeable barrier. It is composed primarily of waxes, alcohols, fatty acids and sugars interspersed within and covering a layer of cutin.[5] Methods have been described both for the isolation of clean intact membranes and for assessing the permeability of these isolated tissues.[5–7] Only very small amounts of soluble inorganic lead salts penetrated isolated cuticles from several economic plants even after six days of exposure.[7] Cuticles from tomato fruit, which are similar in morphology and chemical composition to cuticles from several other economic plant leaves and fruits,[8] were chosen for study. Although the uptake (and deleterious effects) of water-soluble tetra-alkyllead transformation products by the roots of spring wheat has been reported,[9] we are unaware of any studies on the foliar uptake of these compounds by plants.

MATERIALS AND METHODS

Reagents and glassware

All chemicals were ACS reagent grade or better and solvents were distilled-in-glass grade unless otherwise noted. Glassware was made of Pyrex with ground glass joints or Teflon-lined screw caps. $^{210}Pb(NO_3)_2$ (120.4 kBq, 414 MBq mmol^{-1}) was purchased from Amersham International Ltd, Aylesbury, UK.

Synthesis of [^{210}Pb]-$(CH_3)_3PbCl$ (Fig. 1)

Steps A and B

In a 40 cm^3 tube, a neutral aqueous solution of $^{210}Pb^{2+}$ (0.29 μmol, 414 MBq mmol^{-1}) was extracted three times with sodium diethyldithiocarbamate (1 cm^3 mol dm^{-3} NaDEDTC) and diethyl ether (5 cm^3). Phase separation was hastened by centrifugation at 1000g for 1 min. The ethereal phases were combined in a 15-cm^3 graduated centrifuge tube, and cooled to −50 °C in liquid air to solidify residual water; the liquid phase was dried over sodium sulfate (Na_2SO_4), filtered and transferred to a graduated tube and evaporated to 1 cm^3 under a stream of anhydrous nitrogen gas. The extract was then reacted with 20 μL (321 μmol) of CH_3I and 0.5 cm^3 of CH_3MgBr (2.9 mol dm^{-3} in diethyl ether, Aldrich Chemical Co.). The reaction mixture was periodically vortexed during 15 min reaction time at room temperature; then it was cooled to −50 °C and slowly deactivated with the sequential addition of water-saturated diethyl ether (5 cm^3), water (3 cm^3), and 5% nitric acid (2 cm^3). The resulting aqueous phase was removed and washed twice with diethyl ether (3 cm^3). The ethereal phases were combined and dried with Na_2SO_4.

Step C

The dried organic phase containing [^{210}Pb]-$(CH_3)_4Pb$ was transferred to a 25-cm^3 three-necked conical flask fitted with a magnetic stirrer, a condenser–drying tube assembly and a capillary bubbler. The reaction mixture was saturated with a gentle flow of gaseous HCl

(at room temperature) for 2 min, then reacted at 0 °C for 20 min. The crude product mixture was cooled to −50 °C and neutralized with cold aqueous 2 mol dm^{-3} sodium hydroxide (9 cm^3). The aqueous phase containing [^{210}Pb]-$(CH_3)_3Pb^+$ was transferred to a 40-cm^3 tube, adjusted to pH 7–8 (using a piece of pH-paper suspended in the solution), and extracted three times with 5 cm^3 diethyl ether. The organic washes were combined, back-extracted with 5 cm^3 water (which was added to the aqueous fraction), dried over Na_2SO_4, and returned to the reaction assembly (which has been rinsed several times with small volumes of anhydrous diethyl ether). The mono-demethylation of remaining [^{210}Pb]-$(CH_3)_4Pb$ in the ethereal phase was repeated twice.

Steps D and E

The aqueous solution containing [^{210}Pb]-$(CH_3)_3Pb^+$ was extracted twice with diethyl ether (5 cm^3) and aqueous sodium dimethyldithiocarbamate (Aldrich Chemical Co.) (1 cm^3, 3 mol dm^{-3} NaDMDTC). The ethereal extracts were combined, dried (as above), and concentrated to 0.2 cm^3 under nitrogen gas. The crude extract was purified (100 μL injections) by HPLC. Fractions of eluate containing the product were combined, evaporated to 2.5 cm^3 under nitrogen and diluted to 5 cm^3 with 40% acetic acid. The acidic phase was then extracted twice with 3 cm^3 of 4 mmol dm^{-3} dithizone (diphenylthiocarbazone, Dz) in benzene to remove residual ^{210}Bi and excess dithizone. The product was stored at 4 °C.

Radiolytic stability trial

Two aliquots of the product (3.3 kBq) were diluted to 5 cm^3 with 20% aqueous acetic acid and stored at 4 °C in the dark. One of these solutions was extracted every three weeks with 4 mmol dm^{-3} dithizone in benzene (2 × 3 cm^3) to remove ^{210}Bi and ^{210}Po. Both solutions were sampled periodically and analysed by HPLC/liquid scintillation counting (LSC).

High-pressure liquid chromatography (HPLC)

The HPLC system comprised a solvent switching valve, a single piston pump (Beckman model 110A), a rotary injection valve fitted with a 100-μL sample loop (Valco), a guard column (μ-Bondapak ODS, Waters Associates), a 15 cm × 0.416 cm column filled with 5 μ Hypersil ODS (fully end-capped C_{18} reversed-phase, Shandon Laboratories) and a short length of stainless-steel tubing which facilitated the collection of chromatographic fractions. A separation of Pb^{2+}, $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$ in less than 7 min was achieved with the following mobile phases (1 cm^3 min^{-1}) and solvent programme.

Mobile phase A: 85% (v/v) methanol, 5% water, 10% 1,4-dioxane and 150 μg dm^{-3} dithizone;

Mobile phase B: 80% (v/v) methanol, 5% water, 5% glacial acetic acid, 10% 1,4-dioxane and 150 μg dm^{-3} NaDMDTC;

Solvent programme: mobile phase A to time (t) = 0 min, upon injection mobile phase B to t = 6 min followed by mobile phase A until next injection at 16 min.

For preparative chromatography the eluate was collected in 1 cm^3 fractions, which were sampled (10 μL) and assayed by LSC. Analytical chromatographic runs were monitored by collecting 0.16 cm^3 fractions of eluate in scintillation vials, which were diluted with scintillation cocktail (5 cm^3 Universol, ICN) and determined by LSC.

Liquid scintillation counting (LSC)

Scintillation counting was performed with a Rack Beta, Model 1219, liquid scintillation counter (LKB — Wallac, Turku, Finland) equipped with a multichannel analyser providing logarithmic-to-digital conversion to 1024 channels. All counting was performed in 7 cm^3 polyethylene vials. Aliquots of key fractions sampled during the radiosynthesis, storage trial, and cuticle permeability study were analysed for ^{210}Pb and daughters as described previously.[2]

Translocation of ^{210}Pb-$(CH_3)_3PbCl$ and $^{210}Pb^{2+}$ across tomato cuticle

Tomato fruit cuticles were isolated essentially as described by Orgell.[6] Disks (3-cm diameter) of tomato skin were digested, with gentle agitation at 35 °C, with 10 cm^3 of 3% (w/v) pectinase (Sigma Chemical Co.) in 0.1 mol dm^{-3} phosphate buffer (pH 4.18) containing 0.01% (w/v) merthiolate for 24 h. The cuticles were gently washed with deionized water, examined visually for defects and used immediately or stored in 0.01% aqueous merthiolate solution. The osmotic cell consisted of a 18/9 Pyrex ball joint in which the 6 cm connecting tubes had been

bent to form a smooth 90° arc. The isolated cuticle was immobilized between the two halves of the ball joint which was firmly held by a clamp. Distilled–deionized water (2.5 cm^3) was added to the cell compartment exposed to the internal cuticle surface. The second compartment was then monitored for 6 h for water infiltration. If none was detected, radioactive lead solution (2.5 cm^3, 0.1 kBq) was added to the compartment which contacted the external surface of the cuticle and the ends of the cell were covered with aluminium foil. The internal surface compartment was sampled (20 μL) daily and assayed for ^{210}Pb activity by LSC. Each trial was repeated twice.

RESULTS AND DISCUSSION

Synthesis of [^{210}Pb]-$(CH_3)_3$PbCl

The modified synthetic route to [^{210}Pb]-$(CH_3)_3$PbCl and the ^{210}Pb activities observed in fractions from separate stages of the synthesis are presented in Fig. 1 and Table 1, respectively. The key step in the synthesis was the reaction of methylmagnesium bromide (CH_3MgBr) with ^{210}Pb(DMDTC)$_2$ in the presence of methyl iodide (step B) which proved to be efficient (77.5% radiochemical yield), rapid and safer than the previous electrosynthetic approach.[4] The presence of excess CH_3I in the reaction mixture[10] was required to recycle the metallic lead, a by-product of the oxidative reaction between lead(II) and CH_3MgBr (Eqns [1]–[4], summarized in Eqn [5].

$$4CH_3MgX + 2PbX_2 \rightarrow 2[(CH_3)_2Pb(II)] + 4MgX_2 \quad [1]$$

$$2[(CH_3)_2Pb(II)] \rightarrow (CH_3)_4Pb + Pb^0 \quad [2]$$

$$2CH_3X + Pb^0 \rightarrow (CH_3)_2PbX_2 \quad [3]$$

$$(CH_3)_2PbX_2 + 2CH_3MgX \rightarrow (CH_3)_4Pb + 2MgX_2 \quad [4]$$

$$3CH_3MgX + CH_3X + PbX_2 \rightarrow (CH_3)_4Pb + 3MgX_2 \quad [5]$$

The less-than-quantitative activity balance observed for step B (Table 1) suggested that the unreacted ^{210}Pb (21%) was not present in a soluble form, but was possibly in a colloidal metallic state.

The mono-demethylation of $(CH_3)_4Pb$ using HCl gas (Step C), on a micro-scale, had been difficult to control. Because the completion of the reaction required relatively long times (1–2 h), a portion of the product was further demethylated to $(CH_3)_2PbCl$ and to $PbCl_2$ under a variety of reaction conditions. The yield of [^{210}Pb]-$(CH_3)_3$PbCl was virtually quantitative (95%) if the reaction mixture was neutralized

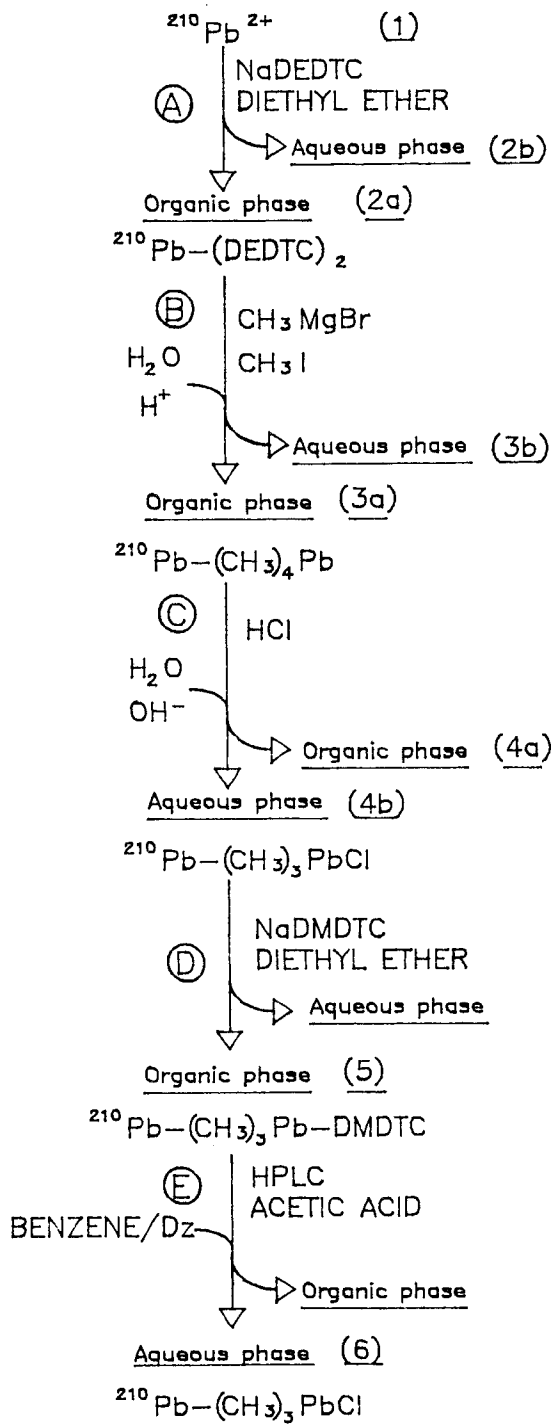

Figure 1 Synthetic route to [^{210}Pb]-$(CH_3)_3$PbCl via a Grignard reaction.

Table 1 Proportion of initial ^{210}Pb activity in key fractions from the synthesis of [^{210}Pb]-$(CH_3)_3PbCl$

Fraction	Activity (kBq)	Percentage of initial activity
1	120.4	100.0
2a	119.9	99.9
2b	0.4	0.3
3a	93.4	77.5
3b	1.8	1.5
4a	88.5	73.5
4b	4.4	3.6
5	87.6	72.8
6	85.5	71.0

after a short period of time (20 min), extracted with water to recover the desired trimethyllead species, dried, and resaturated with HCl gas. This step was repeated twice, until most of the ^{210}Pb activity had been transferred in the aqueous phase. The radiochromatogram of the final product (Fig. 2,B) was essentially free of $^{210}Pb^{2+}$ or [^{210}Pb]-$(CH_3)_2Pb^{2+}$.

Since it was performed in-column, the final purification of the product by HPLC (Step D) was more efficient, facile, and less susceptible to losses than the thin-layer chromatographic (TLC) method previously reported. The TLC purification required that the solid support be removed from the plate and extracted to

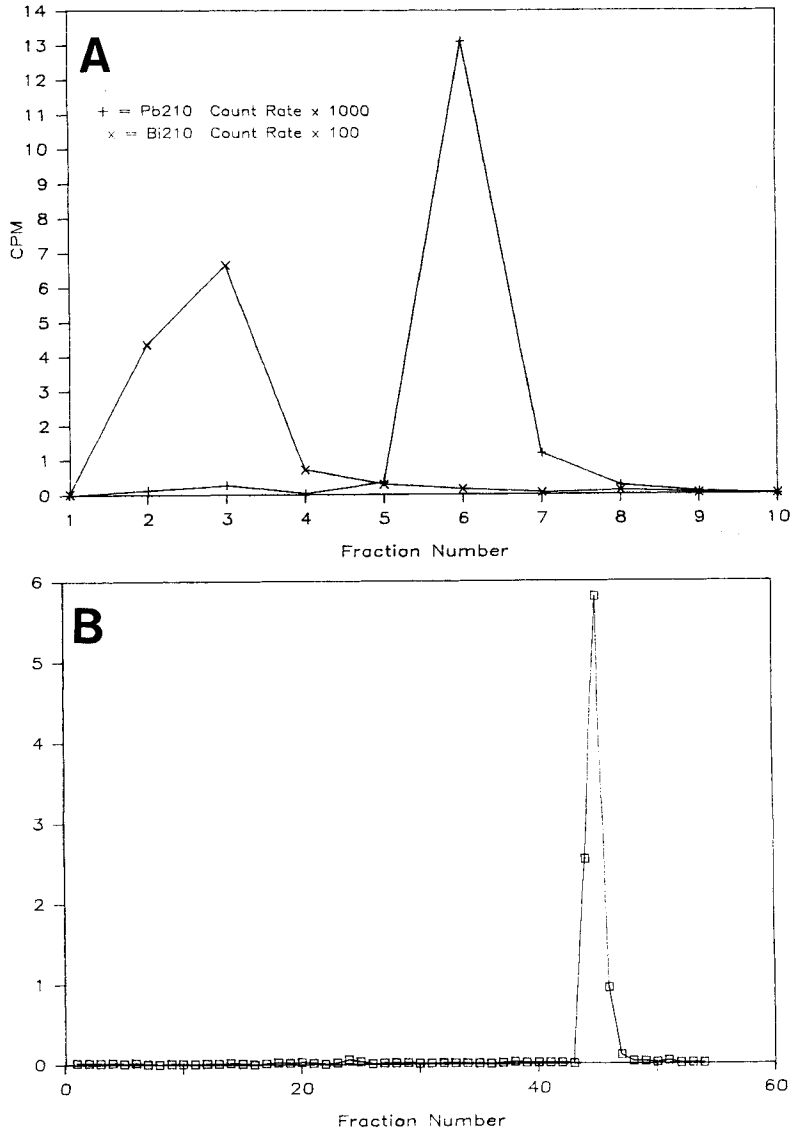

Figure 2 HPLC radiochromatograms: (A) preparative separation of fraction 5 (+, ^{210}Pb count rate × 10^{-3}; ×, ^{210}Bi count rate × 10^{-2}); (B) analytical separations of fraction 6.

recover the product. The ion-pairing HPLC procedure was optimized for preparative or analytical separation of the ionic lead species of interest (Pb^{2+}, R_2Pb^{2+}, R_3Pb^+) and was achieved in less than 7 min (Fig. 2A,B). The addition of complexing agents to the mobile phases (dithizone or DMDTC) was necessary to elute the analytes, which were adsorbed strongly to the Hypersil ODS stationary phase.[11] Although the elution of $(CH_3)_3Pb^+$ occurred only if NaDMDTC was added to the mobile phase, the use of DMDTC alone in the mobile phases did not provide sufficient selectivity for the separation. As demonstrated below, this HPLC system also efficiently separated different physicochemical forms of the ^{210}Pb daughters (^{210}Bi and ^{210}Po) from the lead-210 analytes. Consequently this system was preferable to an equivalent separation of ionic leads which can be achieved on a Nucleosil C_{18} column using isochratic conditions.[11] Appreciable portions of the daughters remained adsorbed on the Nucleosil phase with the APDC solvent system.

HPLC fractions containing the product (Fig. 2A) were combined, concentrated, and adjusted to pH 2–2.5 with acetic acid. At this pH, dithizone is unionized and the excess can be extracted with benzene (as well as $^{210}Bi^{3+}$ and ^{210}Po(IV) dithizonates). At the same time DMDTC (from the HPLC eluant) is rapidly hydrolysed to carbon disulfide (CS_2) and dimethylamine [$(CH_3)_2NH$].[12] Thus, after extraction, the final product can be used for biological studies directly from this solution. Using this synthetic sequence [^{210}Pb]-$(CH_3)_3Pb^+$ was prepared in 71% radiochemical yield. The preparation of radiolabelled dimethyllead would be also possible by modifying the conditions of the dealkylation step (step C).

Since the starting radionuclide ($^{210}Pb^{2+}$) was in secular equilibrium with its daughter nuclides, $^{210}Bi^{3+}$ and $^{210}Po^{4+}$, it was of interest to follow the physicochemical fate of these daughters during the synthesis. Liquid scintillation spectra of samples from key fractions of the synthetic sequence are presented in Fig. 3. As described elsewhere,[2] ^{210}Pb and ^{210}Po spectral energy distributions [channels 49–400 (0.80–28.15 keV) and channels 600–700 (114.3–226.3 keV respectively) are superimposed on a ^{210}Bi broad spectral continuum [channels 49–784 (0.80–400.4 keV)]. Surprisingly, most of the ^{210}Po which was present in the starting material remained in the aqueous phase (Fig. 1, fraction **2b**) after the extraction with NaDEDTC (Fig. 1, step A). Cationic ^{210}Po(IV) is known to form a very stable organosoluble chelate with DEDTC (in a stoichiometry of 1:4).[13] In this case where the original ^{210}Pb solution was neutral, ^{210}Po was not extractable and probably was present in a metallic colloidal form.[1] However most of the ^{210}Bi originally present was carried with the ^{210}Pb through the synthetic sequence (Fig. 3C), reflecting the physicochemical similarities of these elements. Bismuth-210 was partially separated from the product during the chromatographic step (Fig. 2B) and the remainder was complexometrically extracted in the last purification step (Fig. 3D).

Radiolysis of [^{210}Pb]-$(CH_3)_3PbCl$

In the previous study a complete degradation of [^{210}Pb]-$(CH_3)_3PbCl$ to $^{210}Pb^{2+}$ was observed after one year of storage, at −10 °C, in a neutral solution. Since non-radioactive standards maintained under the same storage conditions were degraded by less than 20%, it was concluded that the demethylation of [^{210}Pb]-$(CH_3)_3PbCl$ was the result of a radiolytic process, possibly triggered by α-particles emitted during the radioactive decay of ^{210}Po. Previous results had shown that it was possible to remove ^{210}Pb daughters selectively from a 20% acetic acid solution using a dithizone–benzene complexometric extraction.[2] It was decided to assess this simple technique as a means of preserving the radiolabelled product. Small aliquots (3.3 kBq) of the product, dissolved in 20% acetic acid, were extracted every three weeks so that the product would not be exposed to more than 6.8% of the ^{210}Po activity present at secular equilibrium. Both extracted and unextracted control solutions of $^{210}Pb(CH_3)_3Pb^+$ were chromatographed after six months of storage at 4 °C.

Radiochromatograms of a mixture of $^{210}Pb^{2+}$, [^{210}Pb]-$(CH_3)_2Pb^{2+}$ and [^{210}Pb]-$(CH_3)_3Pb^+$ (100 μL injection from 20% acetic acid) and of the non-extracted control solution (20 μL injection) are presented in Fig. 4. Broadening of the [^{210}Pb]-$(CH_3)_3PbDMDTC$ peak of Fig. 4A resulted from the excessive concentration of acetic acid in the sample. Radiochromatograms of the extracted sample resembled closely the chromatograms of the non-extracted control sample except for the absence of ^{210}Bi and ^{210}Po activity peaks.

Surprisingly the degradation of [^{210}Pb]-$(CH_3)_3Pb^+$ was relatively small. Activity from both the extracted

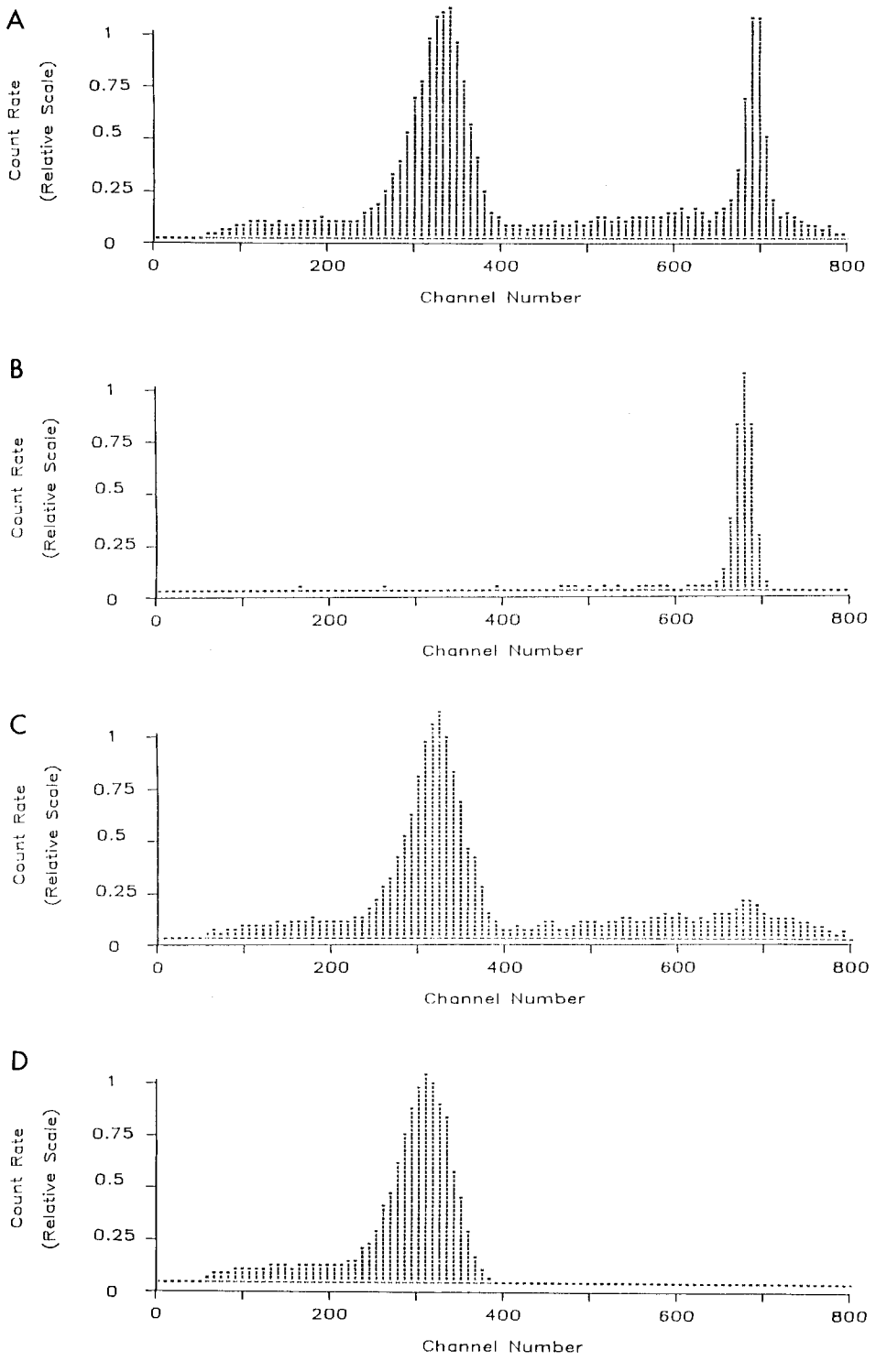

Figure 3 Liquid scintillation spectral energy distributions: (A) $^{210}Pb^{2+}$ secular equilibrium mixture (fraction 1); (B) aqueous phase (fraction 2b); (C) crude [^{210}Pb]-$(CH_3)_3PbCl$ product (fraction 5); (D) purified [^{210}Pb]-$(CH_3)_3PbCl$ (fraction 6).

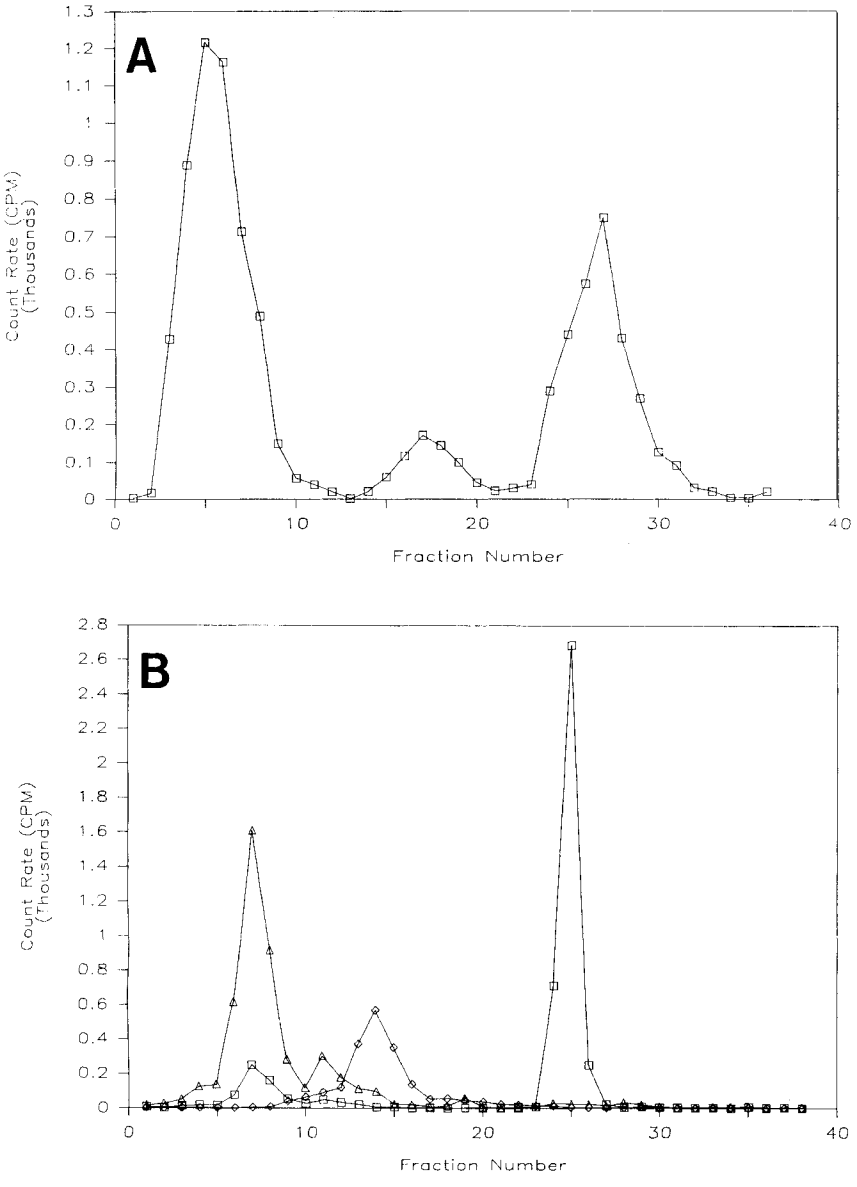

Figure 4 HPLC radiochromatograms of lead-210 (□), bismuth-210 (△), and polonium-210 (◇) activity: (A) synthetic mixture of labelled Pb^{2+}, $(CH_3)_2Pb^{2+}$ and $(CH_3)_3Pb^+$; (B) aqueous solution of [^{210}Pb]-$(CH_3)_3PbCl$ which had been stored at 4 °C for six months.

and non-extracted samples was recovered as [^{210}Pb]-$(CH_3)_3Pb^+$ (85 ± 3%) and $^{210}Pb^{2+}$ (15 ± 4%). A possible explanation for the differences between the current and the previous trial is the relative concentration differences. It is postulated that the relatively slow rate of freezing of the previous sample (at −10 °C) appreciably increased the concentration of the solute near the centre of the flask where freezing occurred last. An appreciable concentration gradient is postulated to have developed which would have accelerated the radiolysis. Alternately, the presence of acetic acid (20% by volume) may have produced a beneficial shielding effect. Regardless of the cause of the increased stability, the product can be stored for at least six months and its radioactive daughters can be removed at the user's discretion.

In the non-extracted control sample (Fig. 4B), ^{210}Bi activity was observed in two rapidly eluting fractions, the major one being co-eluted with the $^{210}Pb^{2+}$ peak. Comparison with radiochromatograms of inorganic $^{210}Pb^{2+}$ (in secular equilibrium with its daughters) indicated that this species was $^{210}Bi^{3+}$. The identity of the second species containing bismuth-210 activity was not established. It may have been a methylated homologue of one of the organobismuth phenylates which have been observed[14] in small proportion (1–16%) during the radiolytic decay of [^{210}Pb]-$(C_6H_5)_4Pb$, [^{210}Bi]-$(C_6H_5)_3Bi^{2+}$, [^{210}Bi]-$(C_6H_5)_2Bi^+$ or [^{210}Bi]-$(C_6H_5)_3Bi$. Polonium-210 activity was observed in a single peak, which co-chromatographed with $^{219}Po^{4+}$. Although ^{210}Bi and ^{210}Po activity balances were estimated from their LSC spectra, the absence of residual activity in the pre-column cartridge and post-chromatographic fractions (using 1% HNO_3 as eluant) suggested that the activities originally present were recovered quantitatively during the chromatography.

Translocation of [^{210}Pb]-$(CH_3)_3PbCl$ and ^{210}Pb across tomato cuticle

The detection of ionic alkylleads in both the gaseous and aerosol phases[15,16] suggests that plants, in the vicinity of major vehicular traffic, may be exposed to appreciable concentrations of these compounds. Since urban gardening remains a popular activity, it was of interest to evaluate the rate of ionic alkyllead uptake by exposed plant surfaces. An initial approach involved a preliminary investigation of the relative rates of transfer of $(CH_3)_3Pb^+$ and Pb^{2+} across isolated tomato cuticle. Cuticles from different plants or from different portions of the same plant were characterized by different permeabilities to Pb^{2+},[7] and the influence of plant exudates, dusts, and other atmospheric deposition on this process has not been studied. Since rates of transfer would be expected to be proportional to the concentration gradient, very dilute solutions were to be used throughout the trials. As suggested by Table 2, there was an appreciable transfer of both toxicants across tomato cuticle over the six-day trial. The translocation of both test chemicals appeared to follow first-order kinetics. A linear regression of time (days) on the logarithm of the difference in activity between the two compartments resulted in a coefficient of correlation (r) of 0.9885 for the Pb^{2+} trial and 0.9608 for the $(CH_3)_3Pb^+$ trial. Appreciably more trialkyllead (75% of the theoretical) than inorganic lead (39%) was transferred. The apparent rate constants (slopes of the regression lines) were 0.0788 and 0.0346 $days^{-1}$ for the alkyllead and inorganic lead respectively). Interestingly, the addition of increasing concentrations of Na_2EDTA (added in 1 mg increments) did not have any measurable effect on the rate of alkyllead transfer over the six-day observation period and only very small amounts of activity were associated with the membrane at the termination of these trials. To the extent that this isolated membrane can serve as a model for fruit surfaces, these preliminary results merit further study.

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Table 2 Translocation[a] of $^{210}Pb^{2+}$ (0.1306 kBq/2.5 cm^3) and [^{210}Pb]-$(CH_3)_3Pb^+$ (0.1136 kBq/2.5 cm^3) across isolated tomato cuticle during six days

Time (days)	Mean cumulative activity transferred (kBq × 10^3)		Mean daily increase (kBq × 10^3)	
	$^{210}Pb^{2+}$	[^{210}Pb]-$(CH_3)_3Pb^+$	$^{210}Pb^{2+}$	[^{210}Pb]-$(CH_3)_3Pb^+$
1	8.1 (7.8, 8.4)	16.0 (15.7, 16.3)	8.1	16.0
2	8.9 (9.0, 8.7)	24.2 (24.3, 24.1)	0.8	8.2
3	13.5 (12.9, 14.0)	34.1 (33.2, 35.0)	4.6	9.9
4	18.3 (18.0, 18.6)	35.2 (35.3, 35.1)	4.8	1.1
6	25.5 (26.1, 24.9)	42.9 (42.4, 43.4)	3.6	3.85

[a]Mean of two replicate experiments (individual observations in parentheses)

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