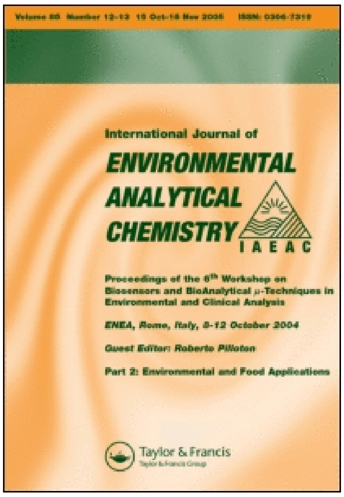

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Texanol Isobutyrate and Other Additive Chemicals—Environmental Contaminants or Laboratory Artifacts?

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Over a period of years, trace organic analysis of Scottish river water and fish samples using gas-chromatography/mass-spectrometry (GC-MS) has often shown the presence of a component with similar elution properties to diethylphthalate and with a dominant ion in the mass spectrum at m/z 71. Closer investigation of this material has now shown it to be 2,2,4-trimethyl-1,3-pentandiol diisobutyrate (common name Texanol isobutyrate), a widely-used industrial chemical marketed as Kodaflex TXIB with applications as a plasticiser, cross-linking agent and lubriciant. The origin of TXIB in analytical samples has been traced to contamination during solvent evaporation operations and it is suggested that a possible source of the chemical might be by slow release into the laboratory atmosphere from vinyl floor coverings. A summary is given of other common contaminants which were identified in the course of these investigations. The genuine occurrence of such materials in environmental samples is not ruled out but these findings highlight the need for rigorous quality assurance in environmental trace analysis if reported levels are to be truly meaningful. A brief assessment of the environmental significance of TXIB is provided.

KEY WORDS: 2,2,4-Trimethyl-1,3-pentandiol diisobutyrate, texanol isobutyrate, Kodaflex TXIB, plasticisers, anti-oxidants, solvent evaporation, contamination, quality assurance, gas chromatography/mass spectrometry, aquatic environment.

INTRODUCTION

Gas-chromatography/mass spectrometry (GC-MS) provides an extremely powerful tool for the analysis of organic chemicals in environmental/biological materials. By virtue of its general lack of discrimination GC-MS presents a more representative picture of the total content of volatile, extractable organic compounds in a sample than that which is typically offered by some of the more selective GC detectors in common use in environmental analysis.

Many of the most widespread and abundant organic chemicals detected by GC-MS in environmental samples constitute simple, man-made materials which are in common, everyday use in bulk-tonnage quantities. The entry of such chemicals into the aquatic environment would usually be the result of a combination of point-source industrial discharges and later, more diffuse release, such as in runoff from residential areas. The range of materials present therefore is generally indicative of modern living and would typically include plasticiser chemicals (particularly the phthalate esters), petroleum hydrocarbon residues, phenolic anti-oxidants, detergent breakdown products, etc. The ubiquitous presence of such chemicals in river water can often give rise to a background GC-MS fingerprint which is to a large extent independent of the actual location from which a sample was taken. Table 1, for example, lists some of the common plasticisers and other industrial materials which were identified in a recent GC-MS survey of organic chemicals in the water of 12 Scottish lowland rivers [1].

CONTAMINATION AND QUALITY ASSURANCE

The fact that many of these background chemicals in the environment represent compounds which are in such widespread use, introduces the very real possibility that samples may become exposed to the same materials during analysis in the laboratory. In the investigation of samples of unknown content therefore, it is extremely important to have good analytical quality assurance. Only in this way is it possible to state with any certainty that an observed component represents a true environmental contaminant and is not simply an artifact introduced during the analytical process.

Table 1 A selection of common industrial contaminants present in Scottish river water which might also be present in laboratory materials

Compound	*R.I.*[a]	*Major m/z*	*Comment/source*
Benzothiazole	1216	108, 135	Rubber additives
Dimethyl phthalate	1448	163, 194	Plasticiser, solvent, insect repellent
2,6-di-*t*-butyl-1,4-benzoquinone	1458	135, 149, 163, 177, 205, 220	Antioxidant and phenolic oxidation product
Butylated hydroxyanisole (BHA)	1483	137, 165, 180	Antioxidant
Butylated hydroxytoluene (BHT)	1506	205, 220	Antioxidant
Diethyl phthalate	1591	149, 177	Plasticiser, solvent, denaturing agent
Tri-*n*-butyl phosphate	1653	99, 155, 211	Plasticiser, solvent
Tris-(chloropropyl)-phosphate (major)	1791	99, 117, 125, 157, 175, 201, 277	Flame retardant plasticisers
(second)	1812	99, 117, 125, 157, 175, 201, 279	
(minor)	1822	99, 117, 125, 157, 175	
Dibutyl phthalate isomer	1843	149, 167, 205, 223	Plasticiser
Dibutyl phthalate isomer	1937	149, 167, 205, 223	Plasticiser
Di-*n*-butyl phthalate	1954	149, 205, 223	Plasticiser, solvent, insect repellent
Sulphur (S8)	1982	128, 160, 192, 256	
Acetyl tributyl citrate	2256	129, 157, 185, 259	Plasticiser
Tris-(dichloropropyl) phosphate	2315	75, 99, 155, 191, 209, 381	Flame retardant plasticiser
Triphenyl phosphate	2380	77, 169, 215, 233, 325, 326	Plasticiser
Di-(2-ethylhexyl) adipate	2390	70, 83, 101, 112, 129, 147, 241, 259	Plasticiser
Tris-(2-butoxyethyl) phosphate	2415	85, 101, 125, 155, 199, 225, 255	Plasticiser, floor polishes

Table I (continued)

Compound[a]	*R.I.*[b]	*Major m/z*	*Comment/source*
Tritolyl phosphate (typical isomer)	2522	118, 251, 353, 368	Plasticiser
Di-(2-ethylhexyl) phthalate	2541	149, 167, 279	Plasticiser, vacuum pump oil
Di-*n*-octyl phthalate	2727	149, 167, 261, 279	Plasticiser

[b] Approximate retention indices based upon a linear interpolation between the elution pattern of *n*-alkanes (RI = $n \times 100$) on a 25m CP-Sil-8 chemically bonded fused silica capillary column.

The introduction of analytical artifacts can be both a systematic or a random process. Systematic contaminant might, for example, arise as a result of the standard addition of solvent which contains the contaminating material as an impurity. Once a problem of this kind has been recognised, it is often relatively straightforward to select suitable method blanks and then to correct the data accordingly. Random artifacts, on the other hand, can sometimes prove more difficult to cope with by standard procedures, either from a qualitative or a quantitative point of view. Heat, light, time of exposure, inhomogeneity of laboratory materials, and many other factors can all give rise to the introduction of contaminants for which it may not be so easy to provide fully adequate quality assurance blanks. For this reason it may be some time before the occurrence of a particular trace organic component is actually recognised to arise as a result of laboratory contamination.

In laboratories which use both GC-MS and GC with other detectors, it is also important to bear in mind that each technique to a large extent requires its own independent quality assurance procedure. Many of the chemicals which can interfere on GC-MS are C,H,O-compounds which do not respond well, if at all, to some of the more selective GC detectors; an acceptable analytical blank run on such a GC system by no means guarantees satisfactory operation on GC-MS.

A wide range of potential sources of contamination in mass spectrometry have been summarised in an extensive review by Ende and Spiteller [2]. Such publications can be extremely useful in dealing with the many analytical contaminants which are common to most laboratories, particularly those from consumables such as solvents, grease, tubing, filter papers, soxhlet thimbles, and so on. The human hand too can be a significant source of spurious chemicals [3] as well as providing a means of transfer of contaminants from other objects handled. In addition it is likely that each individual laboratory will have its own small number of peculiar analytical artifacts, some of which may not have been widely noted in the literature, as was the experience in this laboratory with texanol isobutyrate.

THE IDENTIFICATION OF TEXANOL ISOBUTYRATE

From time to time over a period of years, trace organic analysis in this laboratory using GC-MS has shown the presence of an unidentified component with very similar elution time to diethylphthalate and with a dominant ion in the mass spectrum at m/z 71 (Figures 1, 2). A retrospective examination of GC-MS records has revealed the presence of this material in samples analysed at least as far back as 1982. The widespread appearance of this chemical in environmental samples led to recent speculation that the true source of the material might actually be within the laboratory.

Computer matching of the unknown spectra against the NBS mass spectral library had previously indicated a very close similarity with the compound 2,4,4-trimethyl-1,3-pentandiol diisobutyrate. A subsequent on-line search of Chemical Abstracts, however, failed to locate any reference to this compound from 1967 to the present, a fact which seemed inconsistent with the circumstances under which it was being observed. Further searching identified the isomeric compound 2,2,4-trimethyl-1,3-pentandiol diisobutyrate as an industrial product, with the alternative names Texanol Isobutyrate and Kodaflex TXIB. Texanol is a common/trade name for the corresponding 1- and 3-mono-isobutyrate esters which are described as intermediates in the manufacture of plasticisers, surfactants, urethanes and pesticides [4], whilst Kodaflex is a generic trade name for a group of dialkyl ester plasticiser chemicals including a range of phthalates as well as aliphatic diesters of the adipate, azelate and sebacate type.

A reference sample of Kodaflex TXIB was obtained from the manufacturers, Eastman Chemicals Ltd, and this was confirmed to give a single peak on GC-MS with the same mass spectrum and retention time as the unknown. The predominantly industrial importance of TXIB was further emphasised by the results of a subsequent Chemical Abstracts search, which yielded a total of 72 references, of which no fewer than 54 were in the patent literature. Kodaflex TXIB is marketed as a plasticiser and cross-linking agent, particularly for use in the manufacture of vinyl floor coverings and other high-class PVC products, including toys. In flooring TXIB is incorporated in the uppermost, plastisol layer, often in combination with a phthalate ester plasticiser [5].

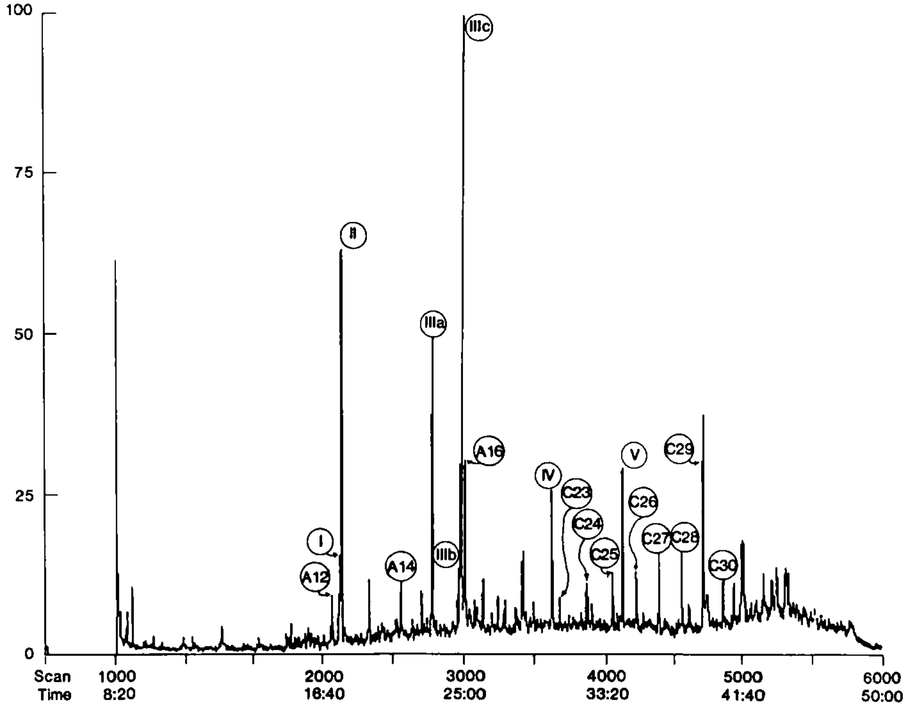

Figure 1 Total ion (70–550 AMU) GC-MS chromatogram of typical river water sample demonstrating contamination by TXIB. An: Straight chain saturated aliphatic acid with *n* carbon atoms. Cn: Straight chain saturated hydrocarbon with *n* carbon atoms. I: Diethylphthalate. II: TXIB. IIIa, b: Dibutylphthalate isomers. IIIc: Di-*n*-butylphthalate. IV: Acetyltributylcitrate. V: Di-(2-ethylhexyl)phthalate. (Splitless injection on 25 m CP-Sil-8 chemically bonded fused silica capillary column.)

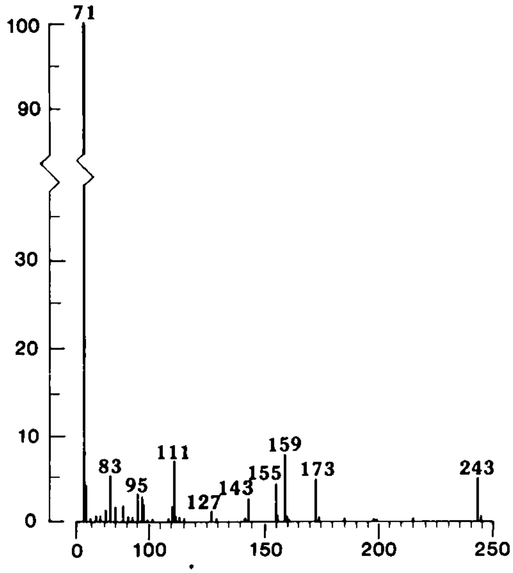

Figure 2 Typical GC-MS electron ionisation mass spectrum (70 eV) of TXIB.

INVESTIGATING THE SOURCE OF TXIB

A review of the normal procedures for the handling of environmental samples in the laboratory led to the postulation of three possible sources of TXIB: solvent impurities; introduction during solvent evaporation; or GC-MS system background contamination. Other processes, such as soxhlet extraction, could also potentially introduce impurities, but these were applied in only a limited number of cases and could not therefore account for the wide range of samples in which TXIB had been positively identified. With this is mind, a detailed series of analytical blanks was run, comparing the level of TXIB contamination in solvents "as received" with that observed following various standard operations in the laboratory. On the basis of these it was clearly demonstrated that the compound was being introduced as a spurious contaminant during routine solvent evaporation operations.

The standard method of sample concentration in this laboratory for many years has been evaporation in a glass tube at atmospheric pressure under a stream of filtered air with minimum warming. The concentration factor for a typical environmental sample for GC-MS would not usually be more than about 100:1, although for some purposes individual samples might be subjected to repeated cycles of evaporation and re-dilution over a longer period of time. In a separate experiment, solvent samples were concentrated in open evaporating dishes on a warmed hotplate to yield GC-MS chromatograms which were essentially free of TXIB contamination, clearly indicating that the compound must be a specific artifact of the evaporative blow-down approach.

There is a report in the literature of instances where attempts to purify solvents by distillation have actually led to an increase in the content of phthalate ester contaminants in the "purified" distillate, a situation which was traced to the pumping of plasticiser chemicals into the laboratoty atmosphere via the air conditioning system [6]. The evidence in this present case also pointed to the idea that TXIB was being delivered in the stream of air supplied by the blower system.

The evaporation apparatus consists essentially of an oil-free compressor pumping filtered laboratory air. Particulates are removed on each side of the pump by passing through soxhlet-type cellulose thimbles before the air is chemically filtered through a customised three-stage tube containing layers of calcium oxide (or similar drying agent), activated charcoal and molecular sieve. The original selection of materials for these filters was made largely on an empirical basis. It can be difficult to decide how often the adsorbents in such filters should best be renewed. Replacing the packing too frequently may lead to increased problems from slow-leaching impurities contained in the adsorbents themselves (despite pre-treatment). Nonetheless, if the filters are used for too long, there is the danger that background contamination in the air supply by a chemical such as TXIB could cause saturation of this component on the column, leading to breakthrough and consequent sample contamination. Close attention to such factors is clearly of considerable importance in the development of a satisfactory overall quality assurance scheme for organic trace analysis.

A variety of materials and components of the apparatus were tested individually as possible sources of TXIB by qualitative extraction/washing procedures (using hexane) but no source was located that could possibly account for the "steady" occurrence of the chemical over a period of years. In fact the only place where TXIB was detected at all was in the inlet filter to the compressor, a fact which seemed consistent with the ultimate conclusion that the chemical must be present in the air of the laboratory itself.

The most obvious long-term source of TXIB in the laboratory environment would appear to be the vinyl floor coverings. One of the characteristic properties of TXIB is its relatively high volatility which has significant consequences for its performance as a component in materials such as PVC sheeting [5]. The upper plastisol layer of the vinyl sheet, is formed at a relatively high temperature (about 200 °C) and, with the large surface to volume ratio, much of the volatile material, including TXIB, is actually lost during the process [7]. TXIB remains at "trace" level in the hardened surface of the sheet, under which conditions it is apparently extremely effective at reducing further plasticiser losses, resisting dirt and also preventing undesirable softening of applied floor polishes [5].

The floors of our laboratory are subject to heavy daily wear, especially during the winter months when they tend to suffer considerable additional abrasion due to salt and grit carried in on outdoor footwear. It is conceivable therefore that there could be slow, irregular transfer of TXIB from the floor coverings into the laboratory air, where it could then act as a fluctuating source of contamination in analytical samples.

The occurrence of volatile organic chemicals in the indoor atmosphere has begun to receive increasing attention in recent years, notably in connection with the U.S. EPA's Total Exposure Assessment Methodology (TEAM) study [8]. Chemical laboratories, however, might potentially present a rather different environment to the homes, offices and public buildings which have been the most common subjects of scrutiny. Weschler and co-workers at Bell Communications have recently carried out surveys of the heavier organics in indoor air of buildings containing a high concentration of electrical apparatus [9, 10]. These studies are particularly useful since they have included consideration of the phase distribution of compounds between vapour, aerosols and particulates. These authors had themselves been alerted to the possibility of TXIB in emissions from carpets, vinyl floor coverings and wall and roof panels [11] and the chemical was indeed detected in one of the buildings investigated in their survey [10], where it was found to be overwhelmingly associated with the vapour phase, rather than adsorbed onto particulate matter.

In our own case an attempt was made to detect traces of TXIB on the surface of the laboratory floor but this failed to confirm the presence of the compound, yielding only a range of contaminants which was considered to be more representative of the applied floor polish than it was of the content of the more resistant plastisol layer. The existence of an alternative source of TXIB cannot, of course, be excluded.

Regardless of its source, the introduction of TXIB into sample extracts during solvent evaporation represents a form of contamination which is, to a large extent, random in nature. The absolute amount of contaminant introduced will depend upon a wide range of variables, such as temperature, solvent volatility, concentration factor, initial and final volume, filter efficiency, level of atmospheric contamination, air flow rate, etc. Some of these factors are essentially uncontrollable in the laboratory environment and it is possible therefore that over a period of time samples could be subjected to widely fluctuating levels of contamination.

OTHER LABORATORY CONTAMINANTS

In the course of the investigation of the source of TXIB in the laboratory a range of other common and potential contaminants were also catalogued and some of these are listed in Table 2. As indicated, a number of these materials also appear amongst the compounds in Table 1 which have been positively identified in the aquatic environment, a fact which has obvious implications for any accurate quantitative work involving these components.

In reality, only a small number of the compounds noted have actually been found to represent what might be termed "unavoidable" contaminants in the context of the work of our laboratory. The most ubiquitous of these materials is undoubtedly di-*n*-butyl phthalate, which is detected in practically every sample analysed and arises at least in part from its presence as an impurity in the solvents used in the laboratory. A further low-level impurity in

Table 2 Summary of laboratory contaminants identified by GC-MS.

Compound[a]	*R.I.*[b]	*Major m/z*	*Comment/source*
C11–C18 and C21–C31 *n*-alkanes (two groups)			Laboratory air, floor, etc.
Decamethyl cyclopentasiloxane	1166	73, 267, 355	Evaporation apparatus
Benzothiazole*	1216	108, 135	Rubber materials
TXIB	1595	71, 111, 155, 159, 173, 243	Laboratory air
Diphenyl amine	1608	168, 169	C6 solvent, as received
N-butyl benzene sulphonamide	1776	77, 141, 158, 170, 213	Soft white nylon tubing
Dibutyl phthalate isomer*	1843	149, 167, 205, 223	Laboratory air
Dibutyl phthalate isomer*	1937	149, 167, 205, 223	Laboratory air
Di-*n*-butyl phthalate*	1954	149, 205, 223	Solvents as received, floor polish, etc.
Di-(2-ethylhexyl) adipate*	2390	70, 83, 101, 112, 129, 147, 241, 259	Evaporation apparatus
C23H3202[c] (?)	2393	177, 284, 340	Rubber materials
Tris-(2-butoxyethyl) phosphate*	2415	85, 101, 125, 155, 199, 225, 255	Floor polish
C25H3602[c] (?)	2487	191, 312, 368	Rubber materials
Di-(ethylhexyl) phthalate*	2541	149, 167, 279	Floor polish
C29H500 sterol (?)	3260	329, 369, 414	Rubber materials
Silicone oligomers (8 compounds)	2446... ...3424	73, 147, 221, 281, 355, 429	GC septum breakdown

[a] "?" denotes an assignment based upon the interpretation of the mass spectral evidence alone. "*" indicates a component which has also been demonstrated as an environmental contaminant (Table 1).

[b] Approximate retention indices based upon a linear interpolation between the elution pattern of *n*-alkanes (RI = *n* × 100) on a 25m CP-Sil-8 chemically bonded fused silica capillary column.

[c] On the basis of their mass spectra, these two compounds have been tentatively identified as a symmetrical methane-bis-(alkylphenol) antioxidants, e.g.: methane-2,2′-bis-(4-methyl-6-*t*-butyl-phenol) and a higher homologue or isomer thereof.

the hexane solvent (Rathburn Chemicals) is diphenyl amine (DPA), which may originate as an amine antioxidant, or perhaps as a breakdown product of a DPA-based dye. Alternatively, it is known that N-nitrosodiphenyl amine (a chemical used as an accelerator in the vulcanisation of rubber) will decompose to DPA on attempted GC analysis [12]. In addition to TXIB, the only other significant impurities likely to be unavoidably introduced into a sample during solvent evaporation appear to be the various di-butyl phthalate isomers and, to a lesser extent, di-(2-ethylhexyl) phthalate (the level of the latter has generally been found to be low in comparison to that typically observed in the environment). N-butyl benzene sulphonamide and di-(2-ethylhexyl) adipate were found to be associated with particular components in the blow-down apparatus and contamination arising from these chemicals could be avoided by careful choice of tubing etc.

THE ENVIRONMENTAL SIGNIFICANCE OF TEXANOL ISOBUTYRATE

The mass spectrum of TXIB, and those of the various phthalate esters, are very characteristic and, unless the peaks actually overlap with other components of interest, the compounds are unlikely to pose any particular problem in routine GC-MS analysis of environmental samples. Even though it is now clear that TXIB is not the ubiquitous pollutant that was first suspected, the existence of a significant source of the compound within the laboratory does not exclude the possibility that the same chemical could also occur as a genuine environmental contaminant. Before concluding these present investigations it was of interest therefore to consider what is known of the environmental occurrence and behaviour of this compound and hence to make an assessment of the likelihood that TXIB analysis would ever be required.

TXIB is used in the manufacture of a number of products which are likely to lead to direct human exposure to significant levels of the chemical, for example from food wrappings, or from plastic toys. US regulations have permitted levels of TXIB equivalent to 10–15% of the final weight of film for use as food wrapping [13, 14] and there is obvious interest therefore in the mammalian toxicology of the material. Feeding and exposure studies have been carried out on rats, mice, dogs and guinea pigs and on the basis of these tests the compound is described as being practically non-toxic, a slight skin irritant and not a sensitiser [15]; acute oral LD50 values for rats and mice were reported to be greater than 3200 and 6400 mg/kg respectively. The only sub-lethal effect noted was a tendency to cause slight increase in the liver weights of rats and dogs fed a diet containing 1 % TXIB. The latter effect has been demonstrated to be reversible in rats on cessation of the contaminated diet [16]. C-14 labelling studies have shown that greater than 95 % of a single dose of TXIB fed to rats is excreted via urine and faeces, most of this within the first 2–4 days [15]. The compound does not appear to be physiologically active, with most of the administered dose being eliminated in the form of unchanged TXIB, or of products arising from the initial loss of one or both of the ester groups [15]; the parent diol was found to be handled by the normal glycol-metabolising pathway leading to the corresponding 1-carboxylic acid.

The manufacturers of TXIB, Eastman Chemicals, state in their product data sheet that the chemical has not been tested for environmental effects [5]. The sheet does, however, provide information on some of the basic chemical and physical properties of the compound. TXIB has a boiling point of 280 °C and its solubility in water at 20 °C is reported to be 0.42 g/litre (420 ppm). The material is almost completely immiscible with water and has a specific gravity of 0.944 [15].

TXIB and its 1- and 3-mono-isobutyrate analogues have been detected at the sub- to low-ppb level in the water of the Delaware River, USA where some of the most comprehensive published GC-MS survey work has been carried out by Hites and co-workers [17, 18]. The exact sources of the compounds in this case were not identified.

TXIB is hydrolysable only to the extent of 0.003 % after 96 h at 100 °C in water [15] and the general evidence would seem to indicate that it is relatively resistant to chemical transformation or to biodegradation. The compound has been detected in drinking water following purification treatment with chlorine dioxide [19], and filtration through soil columns of secondary-treated municipal wastewater containing TXIB led only to a reduction in its concentration from 0.50 ppb to 0.12 ppb [20]. This "recalcitrant" behaviour was ascribed by the latter authors to the relative inability of soil microorganisms to handle branched-chain aliphatic compounds; the observation would further seem to suggest that TXIB would not be subject to strong irreversible binding onto solids in the environment. This would be consistent with the results of other investigations on the removal of trace organics from drinking water, which have shown that the concentration of TXIB in the water was actually increased by filtration through granular activated carbon. By contrast XAD resin was found to reduce the level of TXIB to below the detection limit [21].

The workers at Bell Communications have remarked upon the atypical properties of TXIB, as demonstrated by its marked tendency to partition into the vapour phase in preference to adsorption onto airborne particulate materials, when compared with chemically related compounds of similar molecular weight [10].

Although specific studies on the environmental fate of TXIB are lacking therefore, the overall picture is of a relatively non-reactive chemical which seems unlikely to pose a significant threat at typical residue levels. Human exposure from environmental sources is almost certain to be negligible in comparison to that experienced from other, more direct sources in normal everyday life. The limited metabolism of the compound by mammals, combined with its rapid and almost total excretion, would appear to reduce the toxicological hazard still further.

Since biodegradation of the compound is also slow, it is quite probable that TXIB residues will demonstrate a degree of persistence in the environment, and simple dilution by dispersion and volatilisation may consequently constitute significant pathways in its overall environmental fate.

In terms of work of this laboratory, the only circumstances which would seem likely to give rise to a need to carry out specific analysis for TXIB would be in the event of a particularly large spillage into a watercourse. Such an occurrence would almost certainly give rise to a surface-floating slick, with all the usual implications for oxygen exchange at the air-water interface and the appropriate response would probably be very little different from that for any oxygen-containing organic solvent or similar material. It would seem reasonable to conclude therefore that, at the bulk levels at which TXIB might begin to constitute a major environmental problem, any contribution from trace contamination during analysis would most likely be negligible.

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