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SPECIATION OF ALKYLTIN COMPOUNDS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH A CYANOPROPYL-BONDED SILICA COLUMN

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SUMMARY

A simple, sensitive and selective method has been developed for the simultaneous determination of monoalkyltin homologues. The compounds were separated by high-performance liquid chromatography on a cyanopropyl-bonded silica column with toluene containing acetic acid, methanol, acetonitrile and morin. They were eluted as morin complexes and detected by a fluorescence spectrophotometer. Trialkyltin compounds were separated on the same type of column with hexane containing 0–5% acetic acid and 0–5% ethyl acetate and detected by a refractive index detector. A general study of the behaviour of alkyltins on this type of column was carried out.

INTRODUCTION

Element-specific detection methods, such as spectrophotometry or different polarographic methods, have generally been applied for the determination of both metals and organometallic compounds. Acid or flux decomposition have been extensively used, leaving the metal in an inorganic form. However, the chemistry of metals is determined to a great extent by the groups attached to the metal atom[1]. Better analytical methods are needed for the speciation of various metalorganic compounds. Tin is one of the metals for which this requirement is apparent; it forms compounds with strong metal–carbon bonds and with different biological activities[2].

High-performance liquid chromatography (HPLC) has been applied extensively to the separation of numerous organic compounds, and its use in coordination and organometallic chemistry is growing rapidly[3–5]. These compounds can often be separated and determined quantitatively by HPLC when gas chromatography (GC) is unsuitable because of adsorption and lack of volatility and thermal stability[6,7].

Silica columns, which are used extensively in HPLC with organic and to some extent organometallic compounds[4], are unsuitable for the highly polar organotin compounds, which are almost completely adsorbed on the silica. Jessen *et al.*[8] found that tin tetrachloride and methyltin chlorides could be separated only on the almost inert Styragel column, because of the high reactivity of tin tetrachloride. Alkyltin

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chlorides have been separated on silanized silica, C_2, C_8 and C_{18}, with both acetone–pentane (normal phase)[6,9] and methanol (reversed phase)[10,11] as mobile phase. Aqueous solutions have been applied almost only in connection with strong cation exchangers[12,13]. Cyanopropyl-bonded silica columns have found increased applicability where unmodified silica is unsuitable, and aqueous solutions cannot be used. Dialkyltin compounds have been separated on cyano columns, both as chlorides[14] and as morin complexes[15]. In the latter case morin was incorporated in the eluent, and the dialkyltin complexes were detected by fluorescence spectrophotometry.

The aim of this work was to find conditions for the separation of monoalkyltins in the same way. A general study of the behaviour of alkyltin compounds on a cyano column, both as chlorides and morin complexes, was also undertaken.

EXPERIMENTAL

Reagents

Chemicals were obtained from the following sources: Tri- and dibutyltin chloride from Fluka (Switzerland); tripropyl-, trimethyl- and triphenyltin chloride from the Alfa Division, Ventron Corporation; monobutyl- and triethyltin chloride from ICN Pharmaceuticals, K&K, Rare and Fine Chemicals (New York). Monoethyltin trichloride was synthesized from diethyltin dichloride and tin tetrachloride[16]. Monomethyltin trichloride was made from tin(II) chloride and chloromethane at 360°C[17]. When necessary, the alkyltin chlorides were purified by recrystallization from light petroleum (b.p. 40–60°C) or distillation. The purity of all the alkyltin chlorides was checked by GC. They were pentylated to the tetrapentylalkyltins[18] and analysed on a 3% SP 2250 methylphenylsilicon column. Morin (2′,3,4′,5,7-pentahydroxyflavone) was purchased from Fluka. The toluene was of glass-distilled grade and the hexane of HPLC grade, both obtained from either Rathburn Chemicals or Fison. All HPLC solvents and the morin solution were filtered through 0.45-μm Millipore filters. Helium was used for deaerating the mobile phase.

Apparatus

The HPLC equipment consisted of a Perkin-Elmer dual pump module (Series 2) with a Rheodyne injector, Model 7105, a Perkin-Elmer LC-75 spectrophotometer, a Kontron fluorescence spectrophotometer, Model SFM-23, and a Waters refractive index detector, Model R-401.

Two prepacked cyanopropyl-bonded silica columns (5.0 μm particle size) were used in this study, both obtained from Brownlee Labs.; one stainless-steel column, 250 × 4.6 mm I.D., and one MPLC™ cartridge, 100 × 4.6 mm I.D. The guard column, 30 × 4.6 mm I.D., also containing cyanopropyl-bonded silica (5 μm particle size) was of the MPLC type. The solvent flow-rate was 1.0 ml/min.

Procedure

The alkyltin chlorides were injected as hexane solutions (normally 10 μl). The monoalkyltin chlorides were eluted with toluene containing 5–10% acetic acid, 2% methanol, 2–8% acetonitrile and 5–10 μM morin. Morin is stable in methanol for weeks, and its methanolic solution was added to the eluent. The excitation wavelength

of the fluorescence detector was set at 420 nm and the emission wavelength at 500 nm. When the spectrophotometer was in operation, detection at 420 nm was used. The trialkyltin chlorides were eluted with hexane containing 0–5% acetic acid and 0–5% ethyl acetate.

RESULTS AND DISCUSSION

Separation of monoalkyltin compounds

Dialkyltin compounds have been separated on a cyano column with *n*-hexane–ethyl acetate–acetic acid (90:5:5)[14]. Every attempt at chromatographing monobutyltin trichloride under similar conditions failed. Exchange of hexane for toluene, with the ethyl acetate and acetic acid contents kept at 5%, gave a capacity factor of *ca.* 10. But because methyltin is considerably more polar than butyltin, this way of solving the problem was found not to be promising.

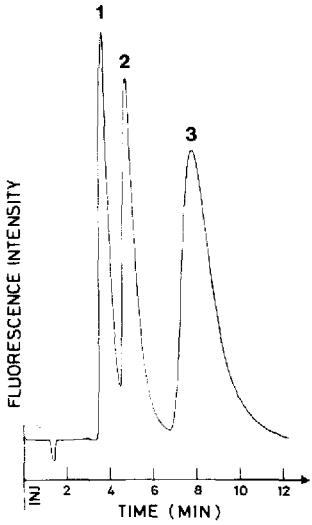
Dialkyltin compounds have been separated by incorporating morin in the eluent and detecting the complexes formed by fluorescence spectrophotometry[15]. A capacity factor of *ca.* 3 was obtained for monobutyltin chloride with 5% of both acetic acid and methanol. However, the peak was much broader than expected from the retention volume. A search for modifiers giving sharper peaks was therefore carried out.

A requirement for the formation of complexes with morin is the ability of the solvent to pick off a proton from the ligand. Methanol, tetrahydrofuran, ethyl acetate, acetonitrile and triethylamine, all representing different selectivity groups[19], were tried. The acetic acid content was held at 5% to reduce the adsorption on residual silanol groups. With triethylamine an infinite tail was observed. A combination of methanol and acetonitrile was found to give the best results. The peaks were, however, still broader than expected from the retention volume.

A morin content of 0.0015% (4.4 μM) was fond to give reproducible and maximum sensitivity for the separation of dialkyltin compounds[15]. Monoalkyltins were, however, much more sensitive to the morin content. The retention volumes decreased to some extent and the peaks became sharper when the amount of morin was increased. An increase of the acetic acid content had the same effect. But in contrast to acetonitrile the effect of varying the morin or acetic acid content depended to a high degree on the condition of the column. On a new column only small differences were observed when going from 5 to 10 μM morin and 5 to 10% acetic acid. Such a change had, however, a considerable influence on the retention behaviour on an older column.

Morin can be exchanged for the less polar ligand 3-hydroxyflavone, which has only one instead of five hydroxy groups. An almost 50% decrease in capacity factor was observed under otherwise unchanged conditions. Morin was selected because of the high fluorescence intensity of the complexes, giving better selectivity and sensitivity.

Fig. 1 shows the separation of monobutyl-, ethyl- and methyltin with an isocratic elution of toluene, 5% acetonitrile, 2% methanol, 5% acetic acid and 5 μM morin. Completely baseline separation between butyl- and ethyltin could be obtained with 2% acetonitrile, but this resulted in a capacity factor of *ca.* 10 for monomethyltin. A better way of solving the problem, if necessary, was to use gradient



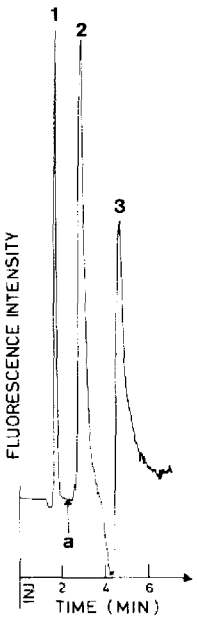


Fig. 1. Separation of monoalkyltin chlorides. Column: (30 + 100) × 4.6 mm I.D., 5 μm, cyano column (Brownlee Labs). Mobile phase: toluene, 5% acetic acid, 2% methanol, 5% acetonitrile and 5 μ*M* morin. Detector: fluorescence spectrophotometer. Peaks: 1 = butyltin trichloride; 2 = ethyltin trichloride; 3 = methyltin trichloride.

Fig. 2. Determination of di- and monoalkyltins in technical tributyltin chloride. Column: (30 + 100) × 4.6 mm I.D., 5 μm, cyano column (Brownlee Labs.). Mobile phase: toluene, 5% acetic acid, 2% methanol, 8% acetonitrile and 5 μ*M* morin. (a) The sensitivity was increased by a factor of 150. Peaks: 1 = dibutyltin (8.1 μg); 2 = monobutyltin (1.5 ng); 3 = monomethyltin (4.0 ng).

elution, starting with 2% acetonitrile and ending with 10% after 10 min. A broad band may be observed for high sensitivities, because of an alternation of the equilibrium of adsorbed morin on the column. The alternation is, however, considerably less than when changing the acetic acid content[15].

Fig. 2 shows the determination of di- and monoalkyltins in technical tributyltin chloride; 8.1% dibutyltin, 0.015% monobutyltin and 0.040% monomethyltin were detected. A GC analysis gave, howver, more than ten times higher monobutyltin and monomethyltin content, showing that a redistribution probably had occurred during GC.

The fluorescence intensity per mole, measured as the peak heights without any column, was 1.0, 1.04 and 2.25 for monomethyl-, monoethyl- and monobutyltin, respectively. The fluorescence intensity of monobutyl- was five times higher that of dibutyltin chloride, whereas the ratio of the absorptivities, measured in the same way at 420 nm, was 1.85. Dibutyltin is found to form mostly a 1:1 complex with both 3-hydroxyflavone and morin. The much higher absorptivity observed for monobutyltin was probably due to the formation of a 1:2 complex with morin. In contrast to the fluorescence intensity, the molar absorptivity is to a high degree determined by the number of ligands in the complex.

The linearity of the calibration graphs was checked by injecting 10 μl of stan-

dards (0.001–100.0 μg/ml) in hexane. They were linear up to more than 1 μg. Detection limits ranged down to 0.7 pg for monobutyltin and 3.0 pg for monomethyltin, depending on the strength of the mobile phase. The "High HV" mode of the detector was used, and the detection limit was taken as twice the noise level.

Deaeration of the mobile phase was omitted because of an increase of the noise level with fluorescence detection[15].

Separation of trialkyltin compounds

In contrast to mono- and dialkyltins, trialkyltins do not form any complexes with either 3-hydroxyflavone or morin in a mixture of toluene or hexane and an alcohol, where the first component is the major one. The conditions used in HPLC require stronger complexes than normally formed by trialkyltin compounds. Methods using pre- or post-column derivatization to form absorbing or fluorescent complexes are therefore not efficient. An element-specific[9,21], an electrochemical[12] or a refractive index detector has to be used.

In this work a refractive index detector was used. Whereas dialkyltin compounds have been separated on a cyano column with *n*-hexane–ethyl acetate–acetic acid (90:5:5)[14], hardly any separation of trialkyltin compounds was obtained under the same conditions. They were eluted almost at the solvent front. Tributyl-, triethyl- and trimethyltin could be separated by reduction of the acetic acid and ethyl acetate contents to 1% each (Fig. 3). The capacity factor of dibutyltin is higher than that of

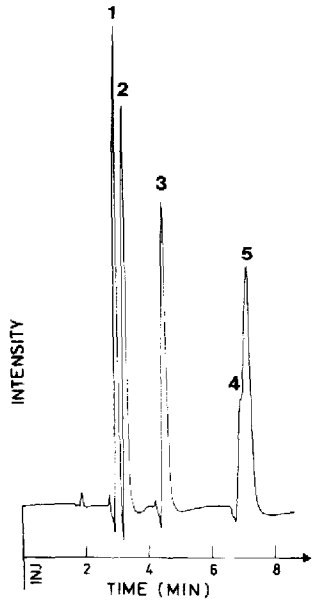


Fig. 3. Separation of trialkyltin and dibutyltin chlorides. Column: (30 + 100) × 4.6 mm I.D., 5 μm, cyano column (Brownlee Labs.). Mobile phase: hexane, 1% acetic acid, 1% ethyl acetate. Detector: refractive index detector. Peaks: 1 = tributyltin; 2 = triethyltin; 3 = trimethyltin; 4 = dibutyltin.

Fig. 4. Separation of trialkyltin and triphenyltin chlorides. Column: (30 + 100) × 4.6 mm I.D., 5 μm, cyano column (Brownlee Labs.). Mobile phase: 100% hexane. Detector: refractive index detector. Peaks: 1 = tributyltin; 2 = tripropyltin; 3 = triethyltin; 4 = trimethyltin; 5 = triphenyltin.

trimethyltin, as shown in the same figure. To obtain complete separation of tributyl- and tripropyltin, 100% hexane had to be used (Fig. 4). The retention volumes of trimethyl- and triphenyltin were almost the same. In pure hexane the methyl compound was eluted first (Fig. 4) whereas the opposite was true when the hexane contained 5% each of ethyl acetate and acetic acid.

Factors determining the retention behaviour

The retention behaviour of organotin compounds on a cyanopropyl-bonded silica column with normal-phase elution is determined by several factors. In addition to the general polarity consideration, the Lewis acid strength of the organotin compounds plays a major part. The acceptor strength[22,23], and therefore the ability to interact with the nitrile groups in the stationary phase, decreases as the number of alkyl groups bonded to the tin atom, increases. Monobutyltin is retarded more than dimethyltin, and dibutyltin more than trimethyltin. The differences do, however, decrease considerably when they are eluted as morin complexes. The retention volume increases with decreasing chain length of the alkyl group for a homologous serie. A distinct difference is observed between the methyl- and ethyltin, and to some extent between the ethyl- and propyltin compounds. The retention behaviour of phenyltin compounds varies, but they always appear after the propyltin compound. The capacity factors of dialkyl- and diphenyltin, when eluted as morin complexes, were found to be higher on a diol column with the same mobile phase. The difference was especially great for diphenyltin, which was eluted long after diethyltin, and for dimethyltin which was not detected within a reasonable time ($k' > 15$).

Broad peaks and tailing were observed for dialkyltins, when eluted as morin complexes, when ethyl acetate and acetonitrile were added to the mobile phase[15]. These modifiers had, however, the opposite effect on monoalkyltins.

In the same way, adsorption on residual silanol groups increases with decreasing chain length and with decreasing number of organic groups bonded to the tin atom. The effect is especially pronounced for monoalkyltin and the methyltin compounds. Very broad peaks and tailing are observed for mono-, di- and trimethyltin. The number of free silanol groups increases as the column ages, and more morin has to be added to make it saturated. A higher content of acetic acid also has to be used to obtain the same results as when the column is new. Because the adsorption effect is most apparent for monoalkyltins, the retention behaviour of these compounds is more sensitive to the condition of the column.

Measurements indicate that monoalkyltins, in contrast to dialkyltins, form 1:2 complexes with morin under the given conditions. There is probably an equilibrium between the 1:2 and 1:1 complexes, which would explain the extremely broad peaks observed for monoalkyltins when eluted as morin complexes. The chromatographic process, when both di- and monoalkyltins are eluted as morin complexes, is probably best characterized as ion-pair chromatography.

Trialkyltin-3-hydroxyflavone, and probably also morin, complexes can be synthesized[20]. However, they decompose on the column, making the trialkyltins undetectable, even when flavonol or morin is added to the mobile phase.

The effect of stainless steel

Tin(IV) is known to be reduced by iron. However, this process with alkyltin

compounds on 316 stainless steel, which most chromatographic equipment is made of, is too slow to have any significant influence on the chromatographic process, although one should be aware of the corrosive effects. It is advisable to inject the sample immediately after loading the injector. The equipment in contact with the tin compounds, especially the injector, should be washed thoroughly after use. A closer examination of the effects of stainless steel and the packing material, on both reduction and redistribution reactions, is to be carried out.

CONCLUSION

The use of a cyanopropyl-bonded silica column and an eluent containing morin as a complexing agent is a very simple, sensitive and selective method for the determination of mono- and dialkyltin compounds. Trace amounts can be detected with just ordinary equipment. Trialkyltin compounds, however, do not form complexes under the given conditions. They can be separated on the same type of column with hexane or with hexane containing small amounts of ethyl acetate and acetic acid as mobile phase. For detection of trace amounts of these compounds an element-specific or an electrochemical detector has to be used. For larger amounts of trialkyltins and for preparative work a refractive index detector does the job.

REFERENCES

1 J. S. Thayer, *J. Organometal. Chem.*, 76 (1974) 265.
2 W. N. Aldridge, *Second Conference on the Organometallic Co-ordination Chemistry of Germanium, Tin and Lead, Organomet. Coord. Chem.*, 9 (1978) 30.
3 B. R. Willeford and H. Veening, *J. Chromatogr.*, 251 (1982) 61.
4 H. Veening and B. R. Willeford, *Advan. Chromatogr.*, 22 (1983) 117.
5 A. R. Timerbaev, O. M. Petrukhin and Yu. A. Zolotov, *Zh. Anal. Khim.*, 36 (1981) 811.
6 D. T. Burns, F. Glockling and M. Harriott, *J. Chromatogr.*, 200 (1980) 305.
7 J. W. Price and R. Smith, *Handbook of Analytical Chemistry, Part III, Vol. 4, Tin*, Springer-Verlag, Berlin, 1978, p. 227.
8 E. B. Jessen, K. Taugbøl and T. Greibrokk, *J. Chromatogr.*, 168 (1979) 139.
9 D. T. Burns, F. Glockling and M. Harriott, *Analyst (London)*, 106 (1981) 921.
10 F. E. Brinckman, W. R. Blair, K. L. Jewett and W. P. Iverson, *J. Chromatogr. Sci.*, 15 (1977) 493.
11 T. M. Vickrey, H. E. Howell, G. V. Harrison and G. J. Ramelow, *Anal. Chem.*, 52 (1980) 1743.
12 W. A. MacCrehan, *Anal. Chem.*, 53 (1981) 74.
13 K. L. Jewett and F. E. Brinckman, *J. Chromatogr. Sci.*, 19 (1981) 583.
14 T. H. Yu and Y. Arakawa, *J. Chromatogr.*, 258 (1983) 189.
15 W. Langseth, *Talanta*, in press.
16 W. P. Neumann, *Ger. Pat.*, 1,177,158 (1962).
17 R. M. Sweet, C. J. Fritchie and R. A. Schunn, *Inorg. Chem.*, 6 (1967) 749.
18 R. J. Maguire and H. Huneault, *J. Chromatogr.*, 209 (1981) 458.
19 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley, New York, 1979, 2nd ed., p. 248.
20 W. Langseth, *Inorg. Chim. Acta*, 90 (1984) 53.
21 M. Ibrahim, T. W. Gilbert and J. Caruso, *J. Chromatogr. Sci.*, 22 (1984) 111.
22 I. R. Beattie, *Quart. Rev., Chem. Soc.*, 17 (1963) 382.
23 R. C. Poller, *J. Organometal. Chem.*, 3 (1965) 321.