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The Determination of Bis(tri-n-butyltin) Oxide and Di-n-butyltin Oxide in Preserved Softwood by Atomic-absorption Spectrophotometry and Polarography

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Methods are described for the determination of the total organotin compounds by atomic-absorption spectrophotometry and for the specific determination of bis(tri-n-butyltin) oxide and di-n-butyltin oxide by atomic-absorption spectrophotometry and polarography. Bis(tri-n-butyltin) oxide and di-n-butyltin oxide are extracted from the wood with hydrochloric acid - ethanol solution and separated from each other and from wood extractives, fungicides and insecticides by adsorption on to Amberlite CG-120 cation-exchange resin followed by elution with solutions containing different concentrations of hydrochloric acid in ethanol.

The procedures have been used to determine bis(tri-n-butyltin) oxide and di-n-butyltin oxide in Scots pine, Corsican pine, Western hemlock, Japanese larch, Sitka spruce, Douglas fir and Western red cedar.

THE fungicidal properties of organotin compounds were first described in the literature in 1954 by van der Kerk and Luijten.[1] In more recent years, bis(tri-n-butyltin) oxide has found increasing use for the protection of timber against fungal attack.[2,3] Bis(tri-n-butyltin) oxide is known in the timber preservation industry as tributyltin oxide or TBTO. The usual form of treatment is carried out by impregnating seasoned wood with solutions of the preservative in organic solvents either by the double vacuum process[4] or the Drilon process,[5] or by application to the surface of the timber by brushing, dipping or deluge. Some preservative solutions contain only TBTO, but in others the organotin may be formulated together with other constituents, *e.g.*, pentachlorophenol, gamma-benzene hexachloride, dieldrin, copper naphthenate, zinc naphthenate, polychloronaphthalene, monochloronaphthalene, *o*-phenylphenol, lauryl pentachlorophenate or water-repellent compounds. It is necessary, therefore, to be able to determine TBTO in the presence of these compounds and wood extractives.

TBTO is a reactive compound and readily forms TBTX compounds with acids, where X is an anion. Wood contains natural phenolic and acidic extractive constituents and it is possible that in treated wood the anions of these compounds replace the oxide radical. Therefore, in this work the tributyltin radical is determined and the results are expressed as TBTO. This approach also applies to di-n-butyltin oxide (DBTO).

The chemical determination of TBTO is needed for the study of the loading and distribution of the preservative achieved by treatment with different processes and preservative formulations and to investigate the permanence of the preservative under various service conditions. Also, because bis(tri-n-butyltin) oxide may be converted into di-n-butyltin oxide *in situ* (*e.g.*, this conversion is known to be caused by ultraviolet light), it is important, for research studies on the permanence of the preservative, to be able to determine separately tributyltin and dibutyltin. In laboratory tests, DBTO was shown to be ten times less toxic than TBTO to fungi.[6] Existing methods for the determination of TBTO are mostly based on the determination of inorganic tin after the decomposition of the organometallic compound. Methods involving the use of X-ray fluorescence spectrometry,[7,8] polarography,[9,10] gas - liquid chromatography,[11,12] thin-layer chromatography,[13] radioactivation analysis,[14] atomic-absorption spectrophotometry,[15] colorimetric techniques[16,17] and titration procedures[18] have been described in the literature for the determination of organotin compounds, but most of these methods are not suitable for the determination of TBTO in wood. Some of the methods

are not specific and give inaccurate results and others are insensitive. Also, because it is difficult to decompose TBTO completely, procedures that involve wet-ashing techniques are slow and tedious.

The initial problem in the development of procedures for the determination of TBTO in timber is the extraction of the organotin compound from wood. Recent work has shown that some preservative chemicals can be rapidly leached from thin sections of wood[19–21] or from sawdust.[22] It has now been found that leaching with a 0·05 per cent. *V*/*V* solution of concentrated hydrochloric acid in ethanol followed by an atomic-absorption spectrophotometric finish affords a rapid method for the determination of total tin in preserved wood. This procedure is suitable for the routine determination of organotin compounds in treated wood when a non-specific method is required.

Because atomic-absorption spectrophotometry is non-specific, an alternative technique was sought for the separate determination of TBTO and DBTO. It is known that organotin compounds are reduced directly at the dropping-mercury electrode,[23,24] which offered the possibility of using a polarographic method. Unfortunately, wood extractives, which are also extracted from the wood during leaching, interfere and it is necessary to separate the organotin compounds from wood extractives before polarographic analysis. This separation was achieved by adsorption of the organotin compounds as chlorides (TBTCl and $DBTCl_2$) on Amberlite CG-120 cation-exchange resin, and by using suitable solvents the TBTCl and $DBTCl_2$ could be eluted separately.

Atomic-absorption spectrophotometry is a more common technique for the determination of preservatives and the polarographic procedures were developed principally as a means of checking the ion-exchange eluates to confirm that separation of TBTCl and $DBTCl_2$ had taken place. Also, they were used to check the results obtained by the atomic-absorption spectrophotometric procedures.

Experimental

Preparation of standard samples and sampling—

Standard samples were prepared by impregnating wood with dioxan solutions containing known amounts of technical grade TBTO, and the full cell process[25] and freeze-drying[26] were used so as to prevent re-distribution and loss of the preservative. The sample blocks were freeze-dried at 0 °C to a residual solvent content of about 6 per cent. and no TBTO was detected in the dioxan condensate. From the observed mass of treating solution retained in the blocks after impregnation, the percentage of TBTO, based on the oven-dry mass of wood, was found by calculation to lie in the range 0·023 to 1·34 per cent.

Despite these precautions, the distribution of TBTO in the treated blocks will not be uniform owing to the anatomical structure of wood. Concentration gradients of TBTO can occur across the annual rings, more being present in the spring or early wood, as the void space is greater, than in the summer or late wood. Therefore, for development work on the procedures, it was decided to use radial sections (cut across the annual rings), as they are more representative of the bulk of the wood. Microtome sections 0·1 mm thick were taken at intervals through the dry block and combined to make one sample for analysis. Adjacent thin sections were taken in order to make up replicate samples. The amounts of the samples taken for analysis were in the range 0·3 to 1 g.

Separation of organotin compounds—

Initially, TBTO was extracted from standard samples with ethanol for polarographic analysis and with isobutyl methyl ketone for atomic-absorption spectrophotometry. Although TBTO was completely recovered from freshly treated timber with these solvents, it was not possible to recover all of the organotin compounds from aged samples and up to 50 per cent. remained in the wood. For complete recovery, the organotin compounds were extracted as the chlorides with a 0·05 per cent. *V*/*V* solution of hydrochloric acid in ethanol. This solvent quantitatively removed the organotin compounds from aged samples and was found to be suitable for atomic-absorption spectrophotometry and cation-exchange procedures.*

The direct polarographic determination of TBTCl and $DBTCl_2$ in the above hydrochloric acid in ethanol leach solutions was not possible owing to interference of the reduction wave

* The ethanol used throughout this work was of 97·5 per cent. concentration.

by wood extractives. In order to separate the TBTCl and $DBTCl_2$ from wood extractives, the organotin compounds were adsorbed on Amberlite CG-120 cation-exchange resin (chromatographic grade, 200 mesh). Direct application of TBTCl and $DBTCl_2$ in a 0·05 per cent. V/V solution of hydrochloric acid in ethanol to columns of resin resulted in only 20 per cent. of the organotin compounds being adsorbed. However, on diluting the leach solution with water (10 ml of water to 20 ml of leach solution), more than 99 per cent. of the organotin compounds was retained. The wood extractives passed through in the initial eluate.

The possibility of separating TBTCl and $DBTCl_2$ on the resin column was also investigated. The elution of the organotin compounds was monitored by polarographic analysis of fractions of the eluate. Separation could not be effected by using different concentrations of hydrochloric acid in ethanol, but it was achieved by varying the water content of the eluting solution. Under the conditions described in the method, it was possible to remove the TBTCl from the resin in less than 10 ml of a solution containing 10 per cent. V/V of water and 0·3 per cent. V/V of hydrochloric acid in ethanol. In solutions that contained 10 per cent. or more of water, only TBTCl was eluted. $DBTCl_2$ was subsequently eluted with 5 per cent. V/V of hydrochloric acid in ethanol. In a solution of this concentration it was possible to remove the $DBTCl_2$ from the resin in less than 10 ml of eluting agent. If a solution containing less hydrochloric acid in ethanol is used, much greater volumes of eluting agent are required in order to elute $DBTCl_2$ from the resin. It is important that the volume of eluate obtained is kept to a minimum so as to avoid loss in sensitivity during atomic-absorption studies with these solutions. The use of this cation-exchange procedure also provides a means of concentrating TBTCl and $DBTCl_2$ from dilute extracts. The separation of wood extractives, TBTCl (expressed as TBTO) and $DBTCl_2$ (expressed as DBTO) is shown in Fig. 1.

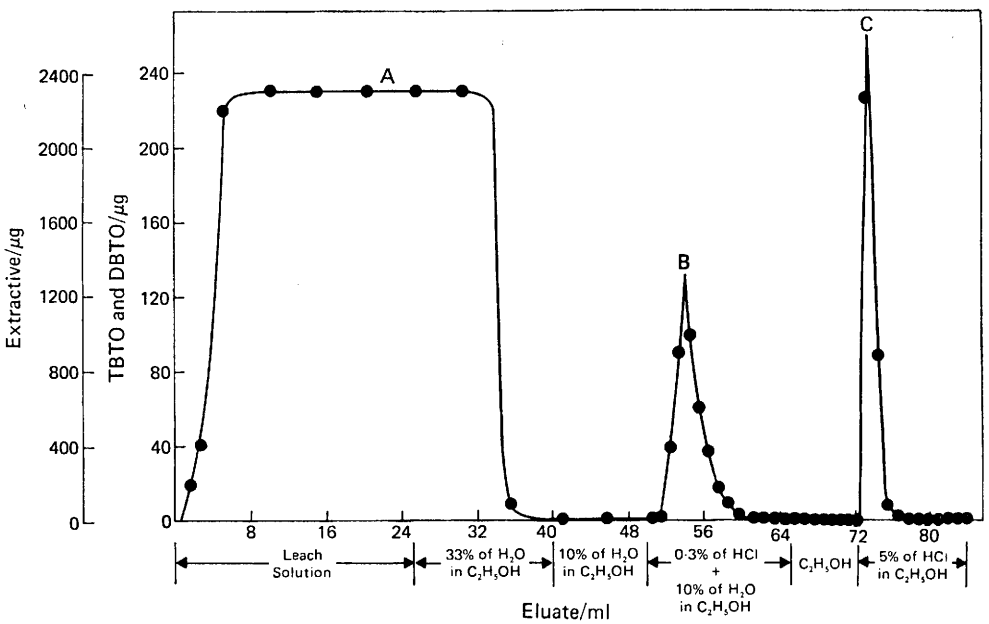

Fig. 1. Elution of (A) wood extractives, (B) TBTCl (expressed as TBTO) and (C) $DBTCl_2$ (expressed as DBTO)

ATOMIC-ABSORPTION SPECTROPHOTOMETRY—

The use of hydrochloric acid in leaching procedures and in ion-exchange separations made it necessary to examine the effect of different concentrations of hydrochloric acid in ethanol in the use of these solutions as media for atomic-absorption spectrophotometry. The absorbance was recorded for solutions containing 20 μg ml^{-1} of TBTO and increasing amounts of hydrochloric acid in ethanol. The results showed that maximum absorbance occurred with solutions containing less than 2 per cent. V/V of hydrochloric acid. Similar

results were obtained for DBTO. Hence the leach solutions consisting of 0·05 per cent. *V*/*V* of hydrochloric acid in ethanol used for the extraction of total organotin give approximately maximum sensitivity. A solution of 5 per cent. *V*/*V* of hydrochloric acid in ethanol was used to elute $DBTCl_2$ from the cation-exchange column. With a solution with this acid concentration a small but acceptable loss in sensitivity occurs.

The use of water in the ion-exchange procedure required that the effect of increasing concentrations of water in a 0·3 per cent. *V*/*V* solution of hydrochloric acid in ethanol on the absorbance signal for tin in TBTO be studied. The results showed that the absorbance signal for tin decreased with increasing concentration of water, but the sensitivity obtained by using a solution of 10 per cent. *V*/*V* of water and 0·3 per cent. *V*/*V* of hydrochloric acid in ethanol was adequate for the levels of TBTO encountered in wood.

Wood contains calcium, potassium, sodium and strontium and some samples of certain species contain lithium. These elements enhance the tin absorbance signal, lithium much more so than the others. This interference is usually observed with Western red cedar, but it occasionally occurs with pines. The interference was effectively overcome by the addition of an excess of lithium (1000 μg ml^{-1}) to the test and calibration solutions in the direct method. The presence of calcium, potassium, sodium and strontium in solutions containing an excess of lithium ions did not affect the tin absorbance signal. The interfering elements are separated from TBTCl and $DBTCl_2$ in the ion-exchange procedure and, therefore, do not influence the equilibrium in the flame between atoms and ions of tin during the specific determination of TBTCl and $DBTCl_2$.

Polarography—

A 2-ml volume of the TBTCl eluate was diluted to 10 ml with a support electrolyte, consisting of 0·94 per cent. *V*/*V* of hydrochloric acid and 2·5 per cent. *V*/*V* of ethanol in 1 M aqueous potassium chloride solution, for polarographic analysis. A similar volume of the eluate containing $DBTCl_2$ was diluted with 1 M aqueous potassium chloride solution for analysis. This dilution ensured that in both test solutions the concentrations of ethanol, hydrochloric acid and potassium chloride were similar. In this electrolyte, $DBTCl_2$ gave two reduction waves at peak potentials of −0·64 and −0·75 V, and TBTCl gave one reduction wave at a peak potential of −0·85 V. Owing to interference to the −0·75 V $DBTCl_2$ reduction wave by the TBTCl reduction wave, it was not possible to use the TBTCl wave for the determination of TBTCl in the presence of $DBTCl_2$. It was possible to determine $DBTCl_2$ in the presence of TBTCl by using the −0·64 V peak.

Effect of other fungicides and insecticides—

Commercial formulations of TBTO wood preservative solutions may also contain other constituents. The effect of the presence of such compounds on the determination of TBTO by atomic-absorption spectrophotometry and polarography was examined. Solutions containing 20 μg ml^{-1} of TBTO and 400 μg ml^{-1} each of pentachlorophenol, lauryl pentachlorophenate, copper naphthenate, zinc naphthenate, *o*-phenylphenol, monochloronaphthalene, polychloronaphthalene and water-repellent waxes, or 40 μg ml^{-1} each of lindane and dieldrin, were examined by the proposed procedures. In the atomic-absorption and polarographic procedures, after cation-exchange separation no interference occurred and complete recovery of TBTO was achieved. Only copper and zinc, from copper and zinc naphthenates, were adsorbed on the resin during cation-exchange separation of the organotin compounds. The ions of these two elements had a more negative reduction potential than TBTCl and caused no interference to the polarographic waves of $DBTCl_2$ or TBTCl. The presence of copper and zinc ions also caused no interference during atomic-absorption spectrophotometry.

Copper and zinc naphthenates caused interference during the direct determination (without ion exchange) of total organotin compounds in leach solutions by the atomic-absorption procedure by enhancing the absorbance signal of tin. The extent of the interference was investigated by preparing two series of solutions, one series containing 20 μg ml^{-1} of TBTO *plus* increasing amounts of copper naphthenate and the other containing 30 μg ml^{-1} of TBTO *plus* increasing amounts of zinc naphthenate. All of the solutions were made up with 0·05 per cent. *V*/*V* of hydrochloric acid in ethanol. The solutions were aspirated and the recorded absorbances plotted against concentrations of either copper naphthenate or

zinc naphthenate (Fig. 2). In both instances the tin signal was enhanced and reached a plateau; similar results were obtained with $DBTCl_2$. This interference can be overcome if an excess of lithium ions is added to both the test and calibration solutions.

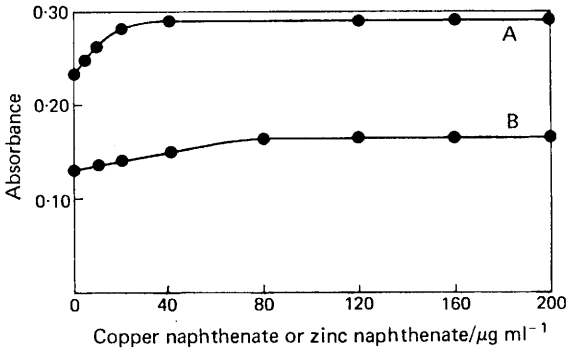

Fig. 2. Interference to tin absorbance signal. Curve A, interference by zinc naphthenate; and curve B, interference by copper naphthenate

ANALYSIS OF TECHNICAL TBTO—

Technical TBTO may contain tri-n-butyltin chloride, di-n-butyltin compounds and solvent. The purity of the technical TBTO used in this work was checked by a polarographic procedure that differed from that previously described. Approximately 0·1 g of TBTO, accurately weighed, was dissolved in ethanol and the solution diluted to 100 ml with ethanol. A 10-ml aliquot of this solution was diluted to 100 ml with a support electrolyte consisting of 6·7 ml of ammonia solution (sp. gr. 0·880), 5·7 ml of glacial acetic acid and 2 ml of 1 per cent. *m/V* Triton X-100 solution, diluted to 1 litre with water. Polarograms were recorded with a Southern Analytical K1000 cathode-ray polarograph with the following instrument settings—

	Start potential/V	Peak potential/V
Bis(tri-n-butyltin) oxide	−1·05	−1·35
Tri-n-butyltin chloride	−0·70	−0·97
Di-n-butyltin oxide (insoluble) ..	—	—
Di-n-butyltin dichloride	−0·80	−1·07
n-Butyltin trichloride	−0·45	−0·71

No $DBTCl_2$ and only trace amounts of TBTCl were detected in the test solution. No reduction wave was observed for DBTO, probably owing to its high insolubility.

In order to detect DBTO, another sample was dissolved in a 5 per cent. *V/V* solution of hydrochloric acid in ethanol and the solution examined for $DBTCl_2$ by the polarographic procedure described later, but only a trace amount of DBTO was found. Therefore, it was concluded that the TBTO used in the preparation of the standard samples was pure and did not introduce any errors in the calculated content of the standards.

RESULTS

The procedures outlined above were used to determine the loading of organotin compounds in standard samples of treated wood. All of the results were based on the oven-dry mass of wood and were expressed as TBTO or DBTO content. The results, given in Table I, were in good agreement with each other and with the calculated TBTO content. Some of the standard samples were examined immediately after they had been freeze-dried. DBTO was not detected in these samples. The remaining samples were examined 6 months after impregnation, and these samples contained both TBTO and DBTO.

The standard deviation, based on seven determinations at the 0·20 per cent. level, was ±0·0039 per cent. for the direct determination of organotin compounds in leach solutions. The standard deviations for TBTO and DBTO, based on seven determinations at the 0·07 per cent. level for TBTO and the 0·0035 per cent. level for DBTO, for the atomic-absorption

TABLE I

LOADING OF ORGANOTIN COMPOUNDS IN STANDARD SAMPLES COMPARED WITH LOADING CALCULATED FROM SOLUTION RETENTIONS

Species	Time of examination	Calculated TBTO content, per cent.	Organotin content by atomic-absorption spectrophotometry, expressed as TBTO, per cent.	After cation-exchange separation: Atomic-absorption spectrophotometry: TBTO content, per cent.	DBTO content, per cent.	DBTO expressed as TBTO equivalent, per cent.	After cation-exchange separation: Polarography: TBTO content, per cent.	DBTO content, per cent.	DBTO expressed as TBTO equivalent, per cent.
Scots pine	Directly after treatment	0·78	—	0·76	Not detected	—	0·77	Not detected	—
Corsican pine		0·39	—	0·39		—	0·39		—
Western hemlock		0·60	—	0·61		—	0·62		—
Sitka spruce		1·12	—	1·11		—	1·10		—
Scots pine		0·038	—	0·040		—	0·039		—
Western hemlock		0·030	—	0·027		—	0·028		—
Japanese larch		0·024	—	0·026		—	0·026		—
Douglas fir		0·026	—	0·028		—	0·027		—
Western red cedar	After storage	1·34	1·35	0·92	0·32	0·38	0·92	0·32	0·38
Scots pine		0·75	0·74	0·72	0·021	0·025	0·72	0·021	0·025
Corsican pine		0·36	0·36	0·35	0·0091	0·011	0·35	0·0088	0·011
Western hemlock		0·62	0·61	0·57	0·036	0·043	0·57	0·036	0·043
Sitka spruce		1·18	1·15	1·10	0·033	0·040	1·10	0·031	0·037
Western red cedar		0·040	0·043	0·029	0·097	0·012	0·030	0·010	0·012
Scots pine		0·038	0·039	0·035	0·0046	0·0055	0·034	0·0047	0·0056
Western hemlock		0·028	0·026	0·024	0·0024	0·0029	0·025	0·0024	0·0029
Japanese larch		0·023	0·024	0·017	0·0050	0·0060	0·018	0·0050	0·0060
Douglas fir		0·027	0·028	0·025	0·0029	0·0035	0·025	0·0029	0·0035

determination after cation-exchange separation were ±0·0010 per cent. for TBTO and ±0·00010 per cent. for DBTO. The standard deviations, based on seven determinations at the 0·20 per cent. level for TBTO and the 0·06 per cent. level for DBTO, for the polarographic technique were ±0·0036 per cent. for TBTO and ±0·00025 per cent. for DBTO.

The atomic-absorption sensitivities were 2 μg ml^{-1} for TBTO in 0·05 per cent. V/V of hydrochloric acid in ethanol, 2·5 μg ml^{-1} for DBTO in 5 per cent. V/V of hydrochloric acid in ethanol and 3 μg ml^{-1} for TBTO in 0·3 per cent. V/V of hydrochloric acid and 10 per cent. V/V of water in ethanol.

To demonstrate the potential value of the proposed atomic-absorption procedure, the distribution of TBTO was investigated in double vacuum treated Scots pine sapwood and in Corsican pine sapwood that had been dip-treated for 3 minutes. Specimens, with surface dimensions of 25 × 25 mm and depth 20 mm, were sawn from the bulk of the treated wood and sections were taken through the radial face in the tangential direction. For the double vacuum treated specimen, starting at the surface, ten thin sections 0·1 mm in thickness were cut on a microtome to form one sample for analysis. The sampling process was repeated to a depth of 12 mm from the surface of the specimen. For the Corsican pine, the first three samples were made up of five thin sections, 0·1 mm in thickness, and the next three samples of ten thin sections, 0·1 mm in thickness. The total organotin content, expressed as TBTO, was plotted against depth of sample. The curves, given in Fig. 3, showed that it is possible to evaluate the distribution of preservative over small areas.

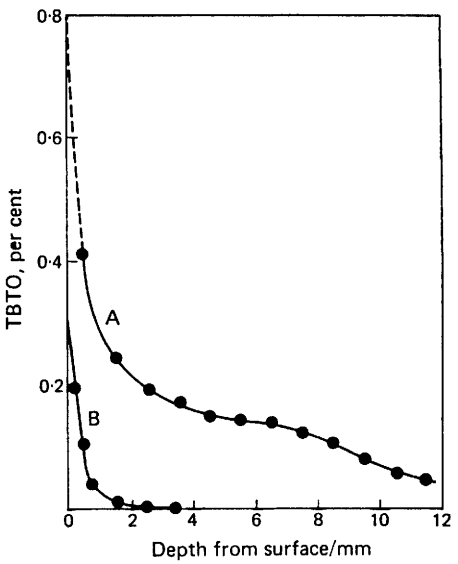

Fig. 3. Distribution of organotin, expressed as TBTO, in (A) double vacuum treated Scots pine sapwood and (B) dip-treated Corsican pine sapwood

The amounts involved would permit the analysis of each 0·1-mm section of the double vacuum treated wood and the first millimetre of dip-treated timber separately so as to obtain a more close distribution pattern. It is also possible to evaluate the conversion of TBTO and DBTO and the distribution of these compounds by using the cation-exchange procedures.

METHODS

Apparatus—

Atomic-absorption spectrophotometry—The atomic-absorption equipment consisted of a Pye Unicam, Model SP90A, Series 2, single-beam spectrophotometer fitted with an EMI No. 9662A photomultiplier and a Pye Unicam, Model AR25, linear recorder. A Cathodeon tin hollow-cathode lamp for use at a wavelength of 224·4 nm was used.

Polarography—Polarograms were recorded with a Southern Analytical Instruments K1000 cathode-ray polarograph and a mercury-pool reference electrode. Solutions were de-oxygenated with oxygen-free nitrogen prior to measurement at 25 ± 0·25 °C.

REAGENTS—

Ethanol—97·5 per cent. Use for the preparation of reagents.

Hydrochloric acid in ethanol, 5 per cent. V/V solution—Dilute 50 ml of concentrated hydrochloric acid to 1 litre with ethanol.

Hydrochloric acid in ethanol, 0·05 per cent. V/V solution—Dilute 10 ml of the 5 per cent. *V/V* solution of hydrochloric acid in ethanol to 1 litre with ethanol.

Hydrochloric acid and water in ethanol, solution containing 0·3 per cent. V/V of hydrochloric acid and 10 per cent. V/V of water—Dilute 3 ml of concentrated hydrochloric acid and 100 ml of water to 1 litre with ethanol.

Water in ethanol, 10 per cent. V/V solution—Dilute 100 ml of water to 1 litre with ethanol.

Water in ethanol, 33 per cent. V/V solution—Dilute 333 ml of water to 1 litre with ethanol.

Hydrochloric acid solution, 20 per cent. V/V—Dilute 20 ml of concentrated hydrochloric acid to 100 ml with water.

Lithium chloride solution, 5000 μg ml⁻¹—Dissolve 3·06 g of anhydrous lithium chloride in and dilute to 100 ml with the 0·05 per cent. *V/V* solution of hydrochloric acid in ethanol.

Support electrolyte 1—Dissolve 7·4600 g of potassium chloride in water and dilute to 100 ml with water.

Support electrolyte 2—Dissolve 7·4600 g of potassium chloride in water, add 0·94 ml of concentrated hydrochloric acid and 2·5 ml of ethanol, and dilute to 100 ml with water.

Cation-exchange resin—Amberlite CG-120 chromatographic resin, 200 mesh.

Bis(tri-n-butyltin) oxide standard solution 1—Dissolve 0·1000 g of bis(tri-n-butyltin) oxide in ethanol, add 5 ml of the 5 per cent. *V/V* solution of hydrochloric acid in ethanol and dilute to 500 ml with ethanol.

1 ml of solution ≡ 200 μg of TBTO.

Bis(tri-n-butyltin) oxide standard solution 2—Dissolve 0·1000 g of bis(tri-n-butyltin) oxide in ethanol and dilute to 500 ml with ethanol.

1 ml of solution ≡ 200 μg of TBTO.

Di-n-butyltin oxide standard solution—Dissolve 0·0500 g of di-n-butyltin oxide in 50 ml of a warm solution of 5 per cent. *V/V* of hydrochloric acid in ethanol, cool, and dilute to 500 ml with the 5 per cent. *V/V* solution of hydrochloric acid in ethanol.

1 ml of solution ≡ 100 μg of DBTO.

Atomic-absorption method for determining organotin compounds—The instrument operating conditions were as follows—

Wavelength	224·4 nm
Slit width	0·05 mm
Attenuator setting	1
Lamp current	7 mA
Scale expansion	Up to × 10
Burner	Nitrous oxide - acetylene
Burner height	0·7 cm
Aspiration rate	3 to 4 ml min⁻¹
Acetylene flow-rate	3800 ml min⁻¹ at a pressure of 0·7 kg cm⁻²
Nitrous oxide flow-rate	5 l min⁻¹ at a pressure of 2·1 kg cm⁻²

CALIBRATION SOLUTIONS

Transfer by pipette, with suitable precautions, 1, 2, 3, 5, 10, 15, 20 and 25 ml of TBTO standard solution 1 into 100-ml calibrated flasks containing 20 ml of lithium chloride solution, dilute to the mark with the 0·05 per cent. *V/V* solution of hydrochloric acid in ethanol and mix. The solutions contain 2, 4, 6, 10, 20, 30, 40 and 50 μg ml⁻¹ of TBTO, respectively.

PROCEDURE—

Transfer the weighed sample into a 50-ml distillation flask. Add 30 ml of the 0·05 per cent. *V/V* solution of hydrochloric acid in ethanol and fit a reflux distillation condenser to the flask. Boil the solution for 10 minutes, cool it to room temperature, decant the leach solution from the wood into a flask, fit a stopper and allow any particles of wood to settle.

Transfer 8 ml of the leach solution into a 10-ml calibrated flask, dilute to the mark with lithium solution and mix.

Use the operating conditions given above and aspirate a suitable range of calibration solutions followed by the sample solution. Do not disturb the sediment during aspiration of the sample solution. Check the calibration solutions after the last sample has been run. Aspirate the 0·05 per cent. V/V solution of hydrochloric acid in ethanol between each test or calibration solution. Plot a calibration graph of the concentration (μg ml^{-1}) of TBTO against absorbance. To determine the TBTO equivalent of the organotin compounds in the sample solution, compare the absorbance reading with the calibration graph.

The volume of the 0·05 per cent. V/V solution of hydrochloric acid in ethanol for leaching the organotin compounds from the wood can be varied according to the amount of sample taken for analysis and its organotin content.

Cation-exchange separation of wood extractives, TBTO and DBTO

Chromatographic column—

A quick semimicro-scale column, of 10 cm effective length and 1 cm bore, with a tap is used. The reservoirs have a capacity of 50 ml.

Preparation of chromatographic column—

Soak the cation-exchange resin in water for 24 hours. Slurry sufficient resin into the column to form a bed 2·5 cm deep when the solids settle down. Elute the column sequentially with 50 ml of 2 M sodium hydroxide solution, water until the eluate is free from alkali, 50 ml of 2 M hydrochloric acid, water until the eluate is free from acid, and finally 20 ml of ethanol. It is necessary to agitate the resin after eluting it with ethanol so as to remove air bubbles. The resin column is now ready for use.

To regenerate the column after each run, elute it successively with 20 ml of 20 per cent. V/V hydrochloric acid solution, water until the eluate is free from acid, and 20 ml of ethanol.

Procedure—

Weigh the sample and transfer it into a 50-ml distillation flask. Add 20 ml of the 0·05 per cent. V/V solution of hydrochloric acid in ethanol and fit a reflux distillation condenser to the flask. Boil the solution for 10 minutes, add 10 ml of water and continue to boil the mixture for 2 minutes. Cool the contents of the flask to room temperature, transfer a suitable aliquot (up to 25 ml) into the chromatographic column reservoir and elute at the rate of 1 drop per 2 s. Rinse the reservoir and elute the resin with 2 volumes of 5 ml of the 33 per cent. V/V solution of water in ethanol, then 5 ml of the 10 per cent. V/V solution of water in ethanol. Elute the TBTCl with the solution of 0·3 per cent. V/V of hydrochloric acid and 10 per cent. V/V of water in ethanol, discard the first 1 ml of eluate and collect the next 10 ml in a 10-ml calibrated flask. Wash the reservoir and elute the resin with 5 ml of ethanol. Elute the $DBTCl_2$ with the 5 per cent. V/V solution of hydrochloric acid in ethanol, discard the first 0·5 ml of eluate and collect the next 10 ml in a 10-ml calibrated flask. The solutions are ready for examination by atomic-absorption spectrophotometry or polarography.

Determination of TBTO by atomic-absorption spectrophotometry

Calibration solutions—

Transfer by pipette, with suitable precautions, 1, 2, 3, 5, 10, 15, 20 and 25 ml of TBTO standard solution 2 into 100-ml calibrated flasks containing 50 ml of ethanol, 10 ml of water and 6 ml of the 5 per cent. V/V solution of hydrochloric acid in ethanol, dilute to the mark with ethanol and mix. The solutions contain 2, 4, 6, 10, 20, 30, 40 and 50 μg ml^{-1} of TBTO, respectively.

Procedure—

Continue as described in the second paragraph of the Procedure (p. 240) for the atomic-absorption method for determining organotin compounds. Aspirate the solution of 0·3 per cent. V/V of hydrochloric acid and 10 per cent. V/V of water in ethanol between each test or calibration solution.

Determination of DBTO by atomic-absorption spectrophotometry

Calibration solutions—

Transfer by pipette, with suitable precautions, 1, 2, 3, 5, 10, 15, 20 and 25 ml of DBTO standard solution into 100-ml calibrated flasks, dilute to the mark with the 5 per cent. *V/V* solution of hydrochloric acid in ethanol and mix. The solutions contain 1, 2, 3, 5, 10, 15, 20 and 25 μg ml^{-1} of DBTO, respectively.

Procedure—

Continue as described in the second paragraph of the Procedure (p. 240) for the atomic-absorption method for determining organotin compounds. Aspirate the 5 per cent. *V/V* solution of hydrochloric acid in ethanol between each test or calibration solution.

Determination of TBTO by polarography

Transfer 2 ml of the TBTO eluate into a 10-ml calibrated flask, dilute to the mark with support electrolyte 2 and mix. Transfer 5 ml of the test solution into a polarographic cell containing a mercury-pool electrode, de-oxygenate for 10 minutes with oxygen-free nitrogen and record the peak current at −0·85 V with a start potential of −0·65 V. To obtain the TBTO content of the test solution, compare the peak current with a calibration graph. Prepare a calibration graph by using the TBTO atomic-absorption standards and the polarographic technique described above.

Determination of DBTO by polarography

Transfer 2 ml of the DBTO eluate into a 10-ml calibrated flask, dilute to the mark with support electrolyte 1 and mix. Transfer 5 ml of the test solution into a polarographic cell containing a mercury-pool electrode, de-oxygenate for 10 minutes with oxygen-free nitrogen and record the peak current at −0·64 V with a start potential of −0·50 V. To obtain the DBTO content of the test solution, compare the peak current with a calibration graph. Prepare a calibration graph by using the DBTO atomic-absorption standards and the polarographic technique described above.

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