CHROMATOGRAPHIC DETERMINATION OF ORGANOTIN COMPOUNDS IN FUNGISTATIC PLASTER

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A method was worked out for the determination of organotin compounds in fungistatic plaster by means of gas and liquid chromatography. The gas chromatographic method is based on chloroform extraction of organotin coumpounds from plaster and on the conversion of these high boiling compounds into more volatile derivatives (chlorides). Analysis by liquid chromatography is carried out directly after extraction with heptane.

INTRODUCTION

Plaster has recently been used on an increasing scale in the production of prefabricated construction elements as it provides the possibility of using gypsum of inferior quality for building purposes now when there is a shortage of building materials. One of the main demands when good quality of prefabricated plaster materials should be maintained is the necessity to protect plaster materials from microbial corrosion. Prefabricated plaster elements are exposed to the risk of infection with fungi and moulds mainly due to their significant contents of water (adsorbed water in the amounts up to 20 %, dihydrate water up to 12—20 % and hydrate water bound to clay materials).

The protection of prefabricated plaster parts against microbial infection can be secured by the addition of small amounts of fungicides of which organic compounds of tin in amounts of 100—1,000 p. p. m. showed to be the most suitable [1]. This fungistatic plaster [2], [3] is intended for the production of prefabricated elements being used in housing and industrial construction, where antifungal preservation is necessary for reasons of hygiene and in many cases is demanded by sanitary regulations. Among organotin compounds, tributyltin acetate, bis-tributyltin oxide, tripropyltin sulphide and tributyltin benzoate appear to be the most efficient fungistatics. A number of these compounds are produced commercially (in Czechoslovakia these are, e. g., products of Lachema N. E., Brno, such as Lastanox). The use of organic tin derivatives in building construction materials also necessitates introduction of standard procedures for their analytical determination in these materials. A photometric method [4] based on dithizone is used for the determination of organotin compounds in building materials. A modification of the original extraction method by Aldridge and Cremer [5] the method requires the use of high purity chemicals. Purification of chloroform, dithizone, ammonia and hydrochloric acid is especially difficult and time consuming. Spectroscopically pure substances or semiconductor-grade ones are mostly required.

The present work describes chromatographic determination of organotin components in commercial preparations of Lastanox F and Lastanox TA, which are used as antifungal additives to plaster for prefabricated construction elements. Separations by gas and liquid chromatography were investigated.

EXPERIMENTAL

Direct extraction from the sample was used for analysing fungistatic plaster. The extraction of organotin compounds from an aqueous suspension was not suitable since it solidifies very quickly in agueous suspension and changes into solid conglomerates of dihydrate from which quantitative extraction of organotin compounds is not praticable.

Both Lastanox F and TA are organotin preparations produced by Lachema, N. E., Brno, Czechoslovakia. While Lastanox TA is pure tributyltin acetate, Lastanox F is a mixture of bis(tributyltin) oxide, aldehydes, surface active substances and other components.

Gas Chromatography

In view of the fact that organotin compounds in plaster (in our case tributyltin acetate or bis (tributyltin) oxide) have high boiling points and the decomposition temperature of tributyltin acetate is 230—250 °C, both organotin compounds, after having been extracted from fungistatic plaster, had to be converted into a compound which could be determined by gas chromatography. Conversion into tributyltin chloride using concentrated hydrochloric acid was selected as the most suitable method. In order to evaluate the transfer quantitatively, the conversion of tributyltin acetate into tributyltin chloride was studied so that a known amount of pure tributyltin acetate was converted into tributyltin chloride in the same way as tributyltin acetate obatined by the extraction of plaster (Tab. I.).

Table I

Conversion of tributyltin acetate into tributyltin chloride

Sample	Weight of tributyltin acetate $g \times 10^{-4}$	Theoretical yield of $SnCl_4$ $g \times 10^{-4}$	$SnCl_4$ found $g \times 10^{-4}$	Conversion %
1.	7.80	6.03	5.86	97.2
2.	7.80	6.03	6.30	104.5
3.	7.80	6.03	5.98	99.5
4.	10.00	7.73	7.37	95.3
5.	5.10	3.84	3.94	102.7

For the extraction, 1.5 g of sample with particle size less than 90 microns was weighed in a 100 ml cuvette, 20 ml of analytical grade chloroform were added and the suspension was agitated for 20 minutes and then centrifugated. The chloroform layer was separated and the residue in the cuvette extracted

again with further 20 ml of chloroform. The suspension was agitated for 5 minutes, again centrifugated and the chloroform layer separated. The sample was transferred on to a filter, washed with a small amount (5—10 ml) of chloroform and all the chloroform extracts were joined. The combined chloroform extracts were evaporated almost to dryness and 3 ml of concentrated hydrochloric acid were added. The mixture was allowed to react for 15 minutes under mild stirring and then transferred quantitatively into a small separation funnel. 5 ml of chloroform were added and the extraction was performed for 10 minutes under continuous agitation. The chloroform layer was transferred into a test tube which was sealed with a teflon stopper.

Tributyltin chloride was determined quantitatively with the aid of a standard (Lachema, N. E., Brno, Czechoslovakia), which was also dissolved in chloroform. The amount of tributyltin chloride found in the treated plaster extract was recalculated for the amount of organotin in the plaster.

Experimental conditions:

gas chromatograph	W. Giede GCHF 18.3. Berlin, GDR
column — length	1 m
— I. D.	0.4 cm
— temperature	160 °C
— packing	10 % Silicone oil DC 200 on Chromaton N-AW-DMCS (equivalent to Chromosorb W-AW-DMCS), 75—90 mesh
detector	flame ionisation detector
gas flow rates — N_2	40 ml/min
— H_2	35 ml/min
— air	600 ml/min
injected amounts	about 5×10^{-7} g

Liquid chromatography

The LC extraction was carried out under the same conditions as the GC one 1.5 g of sample was used, extracted twice, transferred on to a filter and washed. The combined heptane extracts were evaporated almost to dryness and 1 ml of heptane was added to the residue. 30 μl of this solution was injected into the chromatograph.

Experimental conditions:

liquid chromatograph	home-made
column — length	50 cm
— I. D.	0.2 cm
— packing	5 % 1,2,3-tris (2-cyanoethoxy) propane on Chromosorb G (wt/wt), acid washed, 14—21 microns
— temperature	ambient
detector	capacitance detector [6]
mobile phase	degasified *n*-heptane
— flow rate	0.5 ml/min

A damping system described by Locke [7] was used for the suppression of pressure pulses caused by the MC 300 piston pump (Mikrotechna, N. E., Prague, Czechoslovakia). A precolumn packed with 25 % of 1,2,3-tris(2-cyanoethoxy) propane on Chezasorb (equivalent to Chromosorb P) was introduced before the analytical column. Here the mobile phase was saturated with the stationary liquid. The dead volume of the column was determined with *n*-nonane.

RESULTS AND DISCUSSION

Some authors [8] mention a rapid decrease in the detection sensitivity or complete loss of the sensitivity in the course of time if a flame ionisation detector is used. This detector is therefore considered unsuitable for detecting tin compounds. The extracts of organotin compounds from plaster were analysed in the gas chromatograph used for the period of four weeks and in the course of this period no decrease in the sensitivity of the flame ionisation detector was found. Substantial factors influencing the service life of the detector are the amounts of the samples injected and the geometry of the detector.

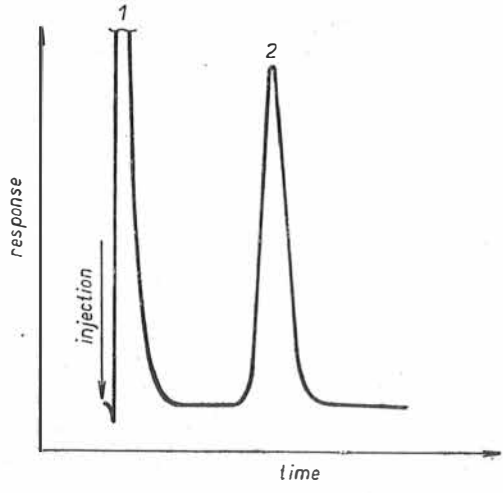

Fig. 1. Model chromatogram of the extract of fungistatic plaster; 1 — chloroform, 2 — tributyltin chloride.

The amount of the sampled tributyltin chloride must be small. It did not exceed 5×10^{-7} g in the course of the analyses of the extracts of fungistatic plaster. The electrodes in the Giede GCHT chromatograph are in the form of two plates positioned in parallel with the flame; the jet does not serve as an electrode. With this geometric arrangement, the detector can be operated without being coated with any substantial layer of tin dioxide for a period of about one month. After three to four weeks of operation, the electrodes (or also the jet) of the detector should be cleaned with a cotton wool pad wetted with distilled water. The service life of the detector in which one of the

electrodes is formed by the jet and the other, collecting electrode, is placed over the burner, is substantially lower.

The sample must not come into contact with water (dilution of the sample, washing of the dish etc.) during the preparation of tributyltin chloride from tributyltin acetate (or bis(tributyltin) oxide) since a reverse hydrolysis of the chloride could occur. The results of the analysis are then either lower or even zero, depending on the extent of the hydrolysis. Teflon stoppers must be used for sealing the test tubes. If rubber stoppers are used, the results of the analyses can be distorted.

Table II

Results of the determinations of tributyltin acetate in fungistatic plaster

Sample number	Amount of tributyltin acetate (p.p. m.)
1	460
2	442
3	428
4	434
5	451
Average	443*

* Manufacturer declares 500 p.p.m.

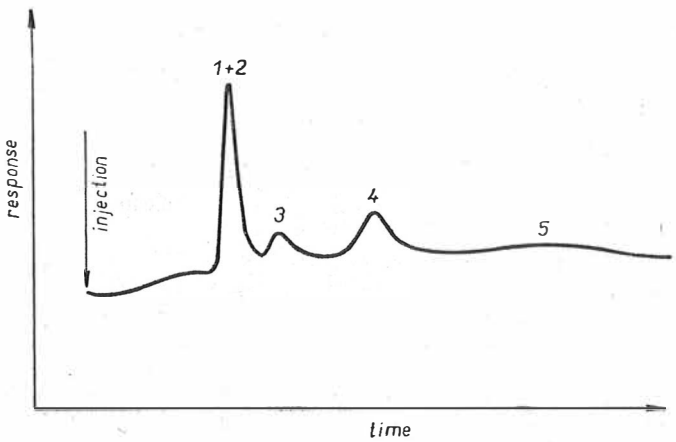

Fig. 2. Chromatogram of Lastanox F; 1 — bis(tributyltin) oxide, 2, 3, 4, 5 — accompanying components.

The results of the analyses of extracts of fungistatic plaster are given in Table II, a chromatogram is shown in Fig. 1.

The application of five percent coating of the support in the case of liquid chromatography is a good compromise between the requirements for sufficient separation of the accompanying components of Lastanox F from bis(tribu-

tyltin) oxide and the speed of the analysis. The separation in the column used is incomplete at lower amounts of tris(cyanoethoxy) propane; at higher amounts, the analysis takes too long. Zero retention of tin compounds is advantageous as far as the detection sensitivity is concerned. It permits a very high analysis speed to be achieved in the case of tributyltin acetate which is the only component of Lastanox TA.

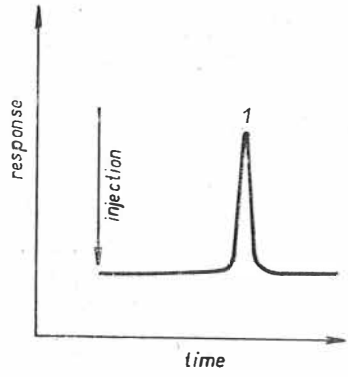

Fig. 3. Chromatogram of bis(tributyltin) oxide; 1 — bis(tributyltin) oxide.

Table III

Analysis of Lastanox F

Sample	Content of bis(tributyltin) oxide in %	Average
1	0.0420 0.0411 0.0416	0.0416
2	0.0408 0.0402 0.0406	0.0405
3	0.0410 0.0405 0.0408	0.0408

Chromatogram of Lastanox F is shown in Fig. 2, that of pure bis(tributyltin) oxide is in Fig. 3. The chromatogram of accompanying components of Lastanox F, showing no antifungal efficiency, is shown in Figure 4. From the comparison of Figures 3 and 4 it follows that one more component of Lastanox F is eluted during the dead volume period. The peak area of this component is about 0.3 % of that of bis(tributyltin) oxide with the detection method used and can therefore be neglected in the analysis.

The results of the determinations of bis(tributyltin) oxide contained in plaster are given in Table III, those of tributyltin acetate in Table IV. Three extracts of Lastanox from plaster were prepared in each case and each of them was analysed three times. The reponse of the capacitance detector to both

bis(tributyltin) oxide and tributyltin acetate is linear with in the 0.005 to 0.050 % concentration range of the analysed substances (i. e. the amount injected after the preparation is $5 \times 10^{-6} - 5 \times 10^{-5}$ g).

The minimum amount which can be determined under these conditions is about 2×10^{-6} g per each injection for both the compounds. Since the amount of organotin compounds in plaster is 10^{-2} % by the order of magnitude, the extract must be prepared in such a manner that the quantity in the sample injected be 10^{-5} g by the order of magnitude (the maximum volume injected for the chromatographic column used is about 30 μl).

Table IV

Analysis of Lastanox TA

Sample	Content of tributyltin acetate in %	Average
1	0.0208 0.0201 0.0203	0.0204
2	0.0209 0.0214 0.0218	0.0213
3	0.0208 0.0209 0.0212	0.0210

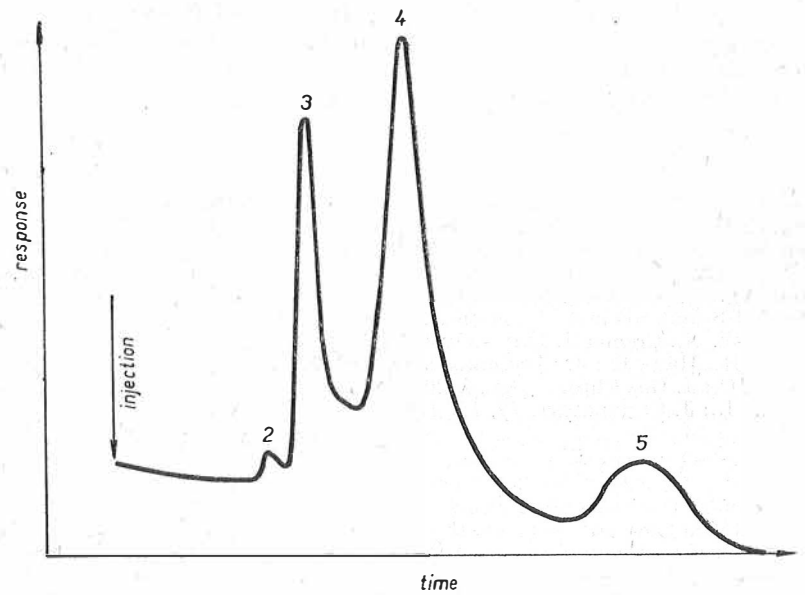

Fig. 4. Chromatogram of accompanying components of Lastanox F; 2, 3, 4, 5 — accompanying components.

The capacitance detector, being a binary concentration detector, reacts also to changes in the composition of of the mobile phase. Since the contents of admixtures differ for various batches of heptane, *n*-heptane of the same batch must be used both as the mobile liquid and for all the extraction and dilution procedures. If n-heptane of another production batch is injected, a false response, caused by a different content of impurities in heptane, can be obtained. The peak thus obtained overlaps the peak of the tin compound under investigation.

The amount of tributyltin acetate found in plaster was 0.021 % (the manufacturer declares 0.020 %) that of bis(tributyltin) oxide was 0.041 % (declared 0.044 %).

A comparison of the two chromatographic methods under investigation shows that the preliminary treatment of samples for the gas chromatographic determination is obviously more elaborate and can be a source of errors. In addition to this, serial measuremens necessitate both electrodes of the detector to be positioned alongside the flame. The high sensitivity of the detection represents an advantage. In the case of analysis by liquid chromatography, the sample treatment is simpler, however, the detection sensitivity is lower. The times necessary for both chromatographic analyses are approximately comparable (about 10 minutes); however, substantial differences arise in the time necessary for the preparation of the sample for chromatographic measurements. This time is two to three times longer in the case of gas chromatography.

By comparing the results of the analyses of fungicides in plaster (see Tables II, III and IV) with the data given by the manufacturer, it can be found that the results differ from the declared values by 10 % at maximum. Taking into consideration that not only the results of the analyses can suffer from the errors (extraction, preliminary teratment of the sample, chromatographic analysis itself) but a also the amount of Lastanox which is assumed to be contained in the plaster (e. g., error in sampling, inhomogeneity of plaster prefabricated products), the agreement is quite acceptable.

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CHROMATOGRAFICKÉ STANOVENÍ ORGANOCÍNIČITÝCH SLOUČENIN VE FUNGISTATICKÉ SÁDŘE

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V článku je popsáno chromatografické stanovení organocíničitých sloučenin ve fungistatické sádře při použití Lastanoxu F a Lastanoxu TA jako antifungálních přídavků.

Při analýze plynovou chromatografií jsou organocíničité sloučeniny (tributylcínacetát a bis-tributylcínoxid) po extrakci chloroformem převedeny koncentrovanou kyselinou chlorovodíkovou na tributylcínchlorid. Roztok chloridu v chloroformu je pak analyzován na plynovém chromatografu s plamenovým ionizačním detektorem, kde jsou elektrody umístěny paralelně s plamenem. Toto uspořádání elektrod zajišťuje „životnost" detektoru pro cíničité sloučeniny nejméně jeden měsíc.

Při analýze kapalinovou chromatografií je extrakce provedena *n*-heptanem a tento roztok přímo analyzován. Vzhledem k tomu, že pro detekci je použito kapacitního detektoru, který reaguje i na změnu složení mobilní fáze, bylo jako mobilní fáze použito *n*-heptanu stejné výrobní série jako při extrakci. Výsledky chromatografických analýz se liší od hodnot udávaných výrobcem nejvýše o 10 %.

Obr. 1. Modelový chromatogram extraktu fungostatické sádry; 1 — chloroform, 2 — tributylcínchlorid.
Obr. 2. Chromatogram Lastanoxu F; 1 — bis-tributylcínoxid, 2, 3, 4, 5 — doprovodné složky.
Obr. 3. Chromatogram bis-tributylcínoxidu; 1 — bis-tributylcínoxid.
Obr. 4. Chromatogram doprovodných složek v Lastanoxu F; 2, 3, 4, 5 — doprovodné složky

ХРОМАТОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ ОЛОВА В ФУНГИСТАТИЧЕСКОМ ГИПСЕ

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В статье описано хроматографическое определение органических соединений олова в гипсе, содержащем Ластанокс Ф и Ластанокс ТА в качестве фунгицидов для консервирования.

При газохроматографическом анализе органические соединения олова (ацетат трибутилолова и окись бис-трибутилолова), во-первых, экстрагируют хлороформом и потом превращают при помощи концентрированной соляной кислоты в хлорид трибутилолова. После того раствор хлорида в хлороформе анализируют на газовом хроматографе, оснащенном пламенно-ионизационным детектором, в котором электроды помещены параллельно с пламенем. Это расположение электродов обеспечивает минимальный срок службы детектора для соединений олова один месяц.

При анализе с помощью жидкостной хроматографии проводят экстракцию *н*-гептаном и полученный раствор берут для анализа прямо. Имея в виду то, что для детектирования пользовались емкостным детектором, который дает отклик и к изменению состава подвижной фазы, в качестве подвижной фазы и для экстракции был использован *н*-гептан той же самой производственной загрузки. Результаты хроматографических анализов отличаются от производственного аттеста максимально на 10 %.

Рис. 1. Модельная хроматограмма экстракта фунгистатического гипса; 1 — хлороформ, 2 — хлорид трибутилолова.
Рис. 2. Хроматограмма Ластанокса Ф; 1 — окись бис-трибутилолова, 2, 3, 4, 5 — сопровождающие компоненты.
Рис. 3. Хроматограмма окиси бис-трибутилолова; 1 — окись бис-трибутилолова.
Рис. 4. Хроматограмма сопровождающих компонент в Ластаноксе Ф; 2, 3, 4, 5 — сопровождающие компоненты.