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Short communication

Evaluation of desulfurization procedures for the elimination of sulfur interferences in the organotin analysis of sediments

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Abstract

Different clean-up and desulfurization procedures were compared in order to check their efficiency in eliminating elemental sulfur and organosulfur compounds from sediment extracts. Adsorption column chromatography cannot remove elemental sulfur or organosulfur compounds. Treatment with activated copper powder only removes elemental sulfur, but organosulfur compounds remain in the extract, and phenyltins are partially lost (up to 50%). Ligand exchange chromatography with $AgNO_3$-coated silica gel as adsorbent effectively removes elemental sulfur and interfering organosulfur compounds from the sediment extract allowing the quantitation of butyltins with recoveries >80%. Since the phenyltin compounds do not survive the desulfurization step, they should be measured in the untreated extract.

Keywords: Desulfurization; Sulfur; Organosulfur compounds; Organotin compounds

1. Introduction

Sulfur, in its elemental state, occurs in anoxic sediments due to microbiological activities which convert sulfates and sulfides to elemental sulfur [1]. It is known that during the derivatization step of sediment extracts with Grignard reagent, alkylation of the sulfur species occurs which mainly leads to the formation of dialkyl mono-, di- and trisulfide [2,3]. Flame photometric detection (FPD), proposed originally for the sensitive and selective detection of organosulfur compounds, has been thought to be very selective for tin if fitted with a red (610 nm bandpass) filter [4,5], but high sulfur concentrations in sediment extracts result in interferences of the alkyl sulfides with the organotin (OT) compounds. Szpunar et al. [6] highlighted the occurrence of high sulfur background and of sulfur compounds in real-life sediments which could affect the analysis of OTs when using tin-selective FPD. Marr et al. [2] warned that those dialkyl sulfides could lead to a misinterpretation as the respective retention time from a pentylated or propylated alkyltin. Cai et al. [3] observed interferences of alkyl sulfides with tin species after hexylation with Grignard reagent. When the OT determination is carried out by gas chromatography–mass spectrometry (GC–MS) in the selected-ion monitoring mode, alkyl sulfides also interfere in their determination. Therefore, an effective meth-

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od for the elimination of elemental sulfur and organosulfur compounds is mandatory for OT speciation analysis.

Common clean-up procedures used in OT analysis consist of an adsorption chromatography step after derivatization with aluminum oxide [7,8], silica gel [7,9,10], Florisil [11–14], or combinations of these materials [15], and hexane as eluent. Clean-up procedures before the derivatization were also applied to OT analysis of sediments using HCl-impregnated silica gel with more polar eluents like hexane–ethyl acetate (4:1) [16]. As the OT species are more stable in tetra-alkylated form, losses can be minimized if the clean-up step is carried out after the derivatization. Therefore, the efficiency of clean-up procedures for the removal of sulfur containing compounds before derivatization has not been evaluated.

Three desulfurization techniques were identified in the literature, (i) selective retention of sulfur on a column packed with activated copper powder [17], (ii) sorption of sulfur by mercury amalgam [18] and (iii) precipitation of sulfur by tetrabutylammonium sulfite [19,20], and adapted to OT analysis [21]. With all of these techniques only elemental sulfur can be removed but the interfering alkyl sulfides remain in the extract [22].

Ligand exchange chromatography was successfully applied to the fractionation of complex mixtures containing sulfur compounds e.g., isolation of sulfur heterocycles from petroleum- and coal-derived materials by $PdCl_2$-impregnated silica gel [23] or isolation of thiophenic compounds from aromatic shale oil fractions by argentation chromatography on a $AgNO_3$-coated silica column [24]. But up to now their efficiency for the separation of alkyl sulfides from OTs has not been evaluated.

The objective of this work was to compare different clean-up procedures after the derivatization to check their efficiency in eliminating organic and elemental sulfur interferences in sediment extracts and to determine the influence of the clean-up procedure on the recovery of the butyl- and phenyltin compounds. In our study pentylated derivatives were used since the shorter the alkyl chain the higher are the volatilization losses during the analytical process [25].

2. Experimental

2.1. Reagents and materials

A test sediment from the Amsterdam channels was received from the Institute for Environmental Studies (IVM) of the Free University of Amsterdam (Netherlands). Furthermore, a marine sediment, collected in the St. Carles de la Rapita marina (western Mediterranean), was used after passing through a 100-μm sieve and freeze–drying.

The highest commercially available grade of monobutyl (MBT), dibutyl (DBT), tributyl (TBT), tripropyl (TPrT), tetrabutyl (TeBT), monophenyl (MPhT), diphenyl (DPhT), triphenyl (TPhT) and tricyclohexyl TCyT) as OT chlorides, and solvents were obtained from different sources.

Neutral aluminum oxide (Al_2O_3, 70–230 mesh), Florisil (60–100 mesh) and silica gel 40 (70–230 mesh) were obtained from Merck (Darmstadt, Germany) and silicic acid (100 mesh) from Fluka (Buchs, Switzerland) and were activated overnight (Al_2O_3 at 120°C, Florisil and silica gel at 60°C and silicic acid at 55°C). Silver nitrate ($AgNO_3$) was obtained from Aldrich (Milwaukee, WI, USA) and copper powder (particle size <63 μm) from Merck.

2.1.1. 25% $AgNO_3$-coated silica gel

Four grams of activated silica gel were mixed with a solution of 1 g $AgNO_3$ in 10 ml MeOH–water (2:1). After 5 min of homogenization in an ultrasonic bath the mixture was allowed to stand in the dark for 1 h. The solvent was eliminated by rotary vacuum evaporation as the bath temperature was increased from 40 to 80°C.

2.1.2. Activated copper

After activating the copper powder by washing under sonication (3–5 min) three times each with 25% HCl, water, acetone and toluene, it was stored under toluene until use.

2.2. Apparatus

A Fisons Mega 2, 8560 model gas chromatograph (Milan, Italy) equipped with an AS 800 autosampler, a DB-17 fused-silica column of 30 m×0.25 mm I.D.,

0.25 μm film thickness (J&W Scientific, Folsom, CA, USA) and a FPD system (FPD 700, Fisons) fitted with a red filter (610 nm bandpass interference filter) was used. Chromatographic conditions are reported elsewhere [26].

2.3. Extraction and derivatization procedures

Six grams of dry sediment were spiked just before the extraction with 1 ml of a 2 ppm TPrT/TCyT solution (400 ng Sn/g sediment) and extracted with a mixture of 12 ml acetic acid and 30 ml toluene by sonicating for 5 min as described elsewhere [26]. The derivatization was performed with 2.0 *M* PeMgBr in diethyl ether.

Standard solutions for the calibration were derivatized in the same way as the sediment extracts. In order to control the efficiency of the following clean-up procedures 1 ml of 1% sulfur in toluene was added to the standard solutions before the derivatization.

2.4. Clean-up procedure

2.4.1. Clean-up columns

The clean-up columns (5 mm I.D.) were conditioned with toluene using activated column adsorbents. Afterwards, 2 ml of the solution of the derivatives in toluene were passed through the column and the analytes were recovered with 5 ml hexane or 10 ml of 50% CH_2Cl_2 in hexane, respectively. Table 1 summarizes the column packings, amounts, activation temperatures and eluents used.

The clean-up column packed with 25% $AgNO_3$-coated silica gel was covered with aluminum foil to prevent darkening of the column material, since $AgNO_3$ is light sensitive.

2.4.2. In situ sulfur elimination in the vial

Approximately 400 mg of activated copper or 100 mg of 25% $AgNO_3$-coated silica gel, respectively, were put into the vials containing the concentrated extract (1 ml) which had been passed through a conventional clean-up column packed with Al_2O_3. After sonicating for 10 min the mixture was allowed to stand for 2 h at room temperature (25% $AgNO_3$-coated silica gel) or overnight in the refrigerator (activated copper).

2.5. Detection and quantitation

TeBT was used as the internal standard. Calibration curves for each OT compound related to TeBT were found to be linear within 10% deviation from the calibration line in the range of 40 to 1600 pg Sn injected into the GC–FPD system. For quantitation, calibration curves of 25 to 300 g Sn/g in toluene (50 to 600 pg Sn absolute injected into the GC–FPD system) were obtained by daily derivatization of 0.5 g of the 50 g Sn/g working solution and subsequent dilution.

3. Results and discussion

We examined different clean-up procedures including adsorption column chromatography and ligand exchange chromatography and treatment with activated copper for their efficiency in removing elemental sulfur and alkyl sulfides from sediment extracts and evaluated the recoveries of butyltins and phenyltins. The recoveries for the clean-up procedures were evaluated with a derivatized standard solution with elemental sulfur added prior to de-

Table 1
Column packings, activation temperatures, amounts and eluents used in the comparison of the clean-up columns

Column packing	Activation temperature (°C)	Amount (g)	Eluent	Volume (ml)
Al_2O_3	120	3	Hexane	5
Florisil	60	2.5	Hexane	5
Al_2O_3/silica gel	120/60	1.5/1	Hexane	5
Silicic acid	55	1.5	Hexane	5
25% $AgNO_3$-coated silica gel	80 under vacuum	2	50% CH_2Cl_2 in hexane	10

rivatization. Fig. 1 shows the recoveries of the OTs for each clean-up procedure evaluated in this work.

3.1. Adsorption column chromatography

The most common clean-up procedures in OT analysis use columns packed with adsorption materials such as Al_2O_3, silica gel, Florisil or combinations of these materials. Different clean-up columns packed with Al_2O_3, Florisil and combined Al_2O_3/silica gel and, besides these, silicic acid as an adsorption material with higher polarity were examined. Standard solutions, with elemental sulfur added before the derivatization, and sediment extracts containing elemental sulfur originally were chromatographed (see Table 1) and all OT compounds were eluted quantitatively with 5 ml hexane yielding recoveries of over 90% (see Fig. 1), but none of the examined columns could remove or separate the interfering alkyl sulfur compounds and the elemental sulfur which coelute with the analytes.

Fig. 2a and Fig. 3a show chromatograms of derivatized sediment extracts chromatographed over Al_2O_3. Beside the huge peaks of dipentyl mono-, di- and trisulfide which interfere with the butyltins, a broad peak of elemental sulfur appears which was neither alkylated during the derivatization step nor eliminated quantitatively by the Al_2O_3 clean-up column. The magnitude of this peak is very irreproducible and depends strongly on the performance of the clean-up step.

Silicic acid showed no clean-up effect on the sediment extract at all, as the colored pigments and other contaminations passed through the column without any retention and therefore could not be separated from the analytes.

Since the common clean-up procedures showed no separation of the OTs and the alkylsulfur com-

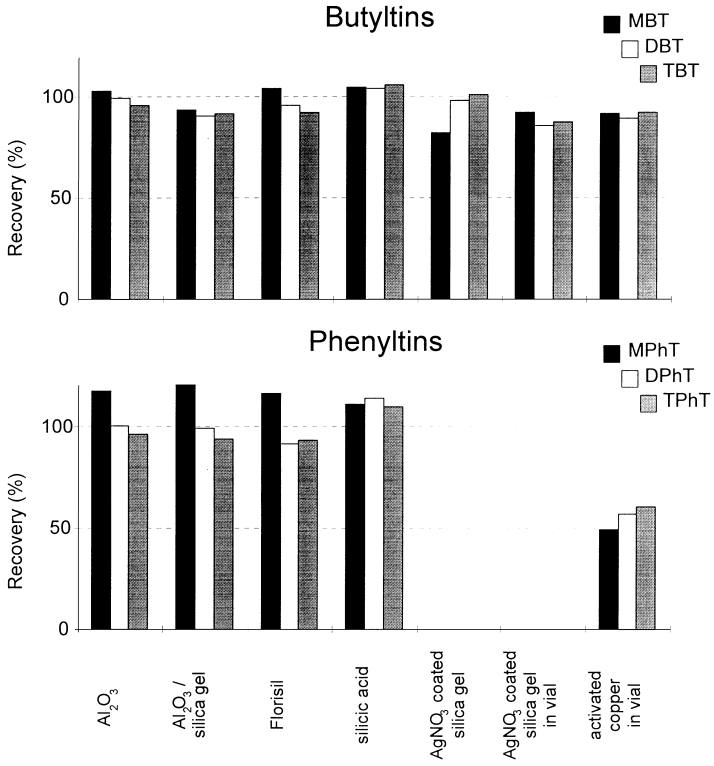

Fig. 1. Recoveries of butyl- and phenyltins in derivatized standard solutions with elemental sulfur added prior to derivatization using different clean-up methods (extraction step not included) (phenyltins in the case of $AgNO_3$ treatment were not recovered).

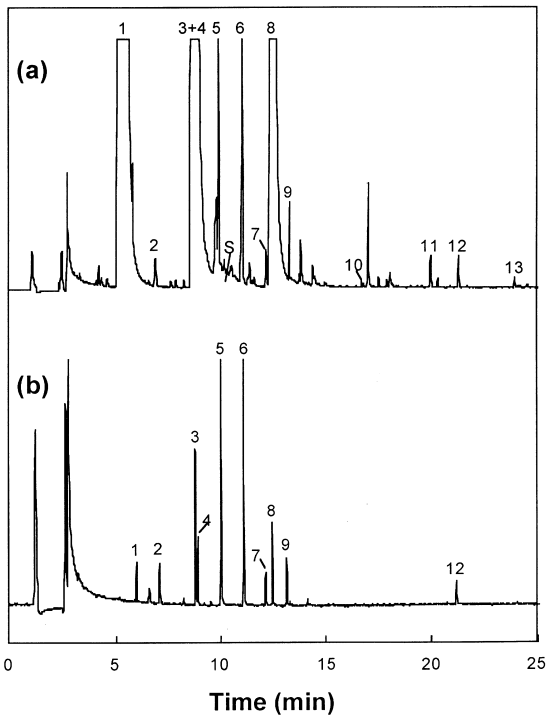

Fig. 2. (a) Gas chromatogram of a derivatized extract of the marine sediment after a conventional Al_2O_3 clean-up column showing high amounts of alkyl sulfides and elemental sulfur. (b) Gas chromatogram of the same extract as in (a) after a clean-up column with 25% $AgNO_3$-coated silica gel. (The scale of the signal axis of the chromatograms is normalized to the height of peak 5, TBT). Compound identification: 1=Pe_2S, 2=TPrT, 3=Pe_2S_2, 4=TeBT, 5=TBT, 6=DBT, 7=MBT, 8=Pe_2S_3, 9=TPeT, 10=MPhT, 11=DPhT, 12=TCyT, 13=TPhT, S=elemental sulfur.

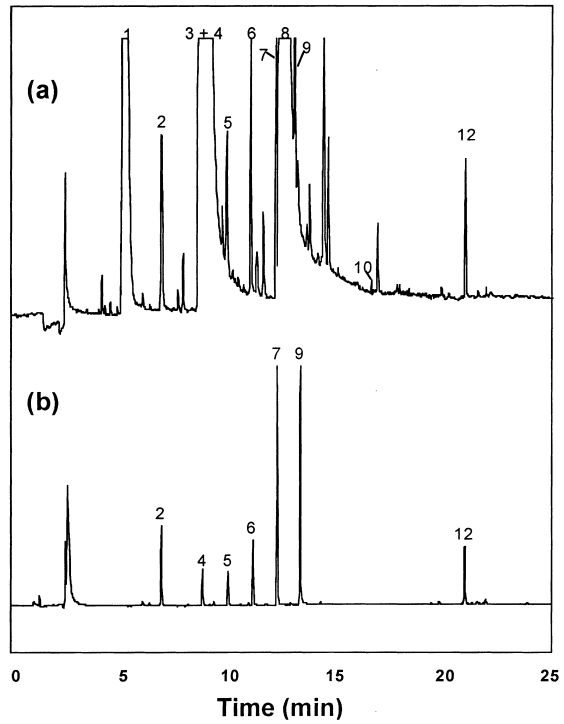

Fig. 3. (a) Gas chromatogram of a derivatized extract of the test sediment after a conventional Al_2O_3 clean-up column showing high amounts of alkyl sulfides. (b) Gas chromatogram of the same extract as in (a) treated with $AgNO_3$-coated silica gel directly in the vial after a conventional Al_2O_3 clean-up column. (The scale of the signal axis of the chromatograms is normalized to the height of peak 6, DBT). Compound identification as in Fig. 2.

pounds, another method using ligand exchange chromatography was examined.

3.2. Ligand exchange chromatography

The elimination of sulfur compounds with ligand exchange chromatography is based on the formation of coordinative bonds between sulfur and metal ions using salts of mercury, copper, zinc or other metals. Argentation chromatography using $AgNO_3$-coated silica gel or chromatography with $PdCl_2$-impregnated silica gel were applied successfully to the isolation of sulfur heterocycles [23]. However, they have not been evaluated in case of desulfurization in the presence of OT compounds.

Using adsorption chromatography with 25% $AgNO_3$-coated silica gel, all interfering sulfur compounds of the derivatized sediment extract (in this case a marine sediment with comparable high amounts of elemental sulfur as in the test sediment was used) were removed quantitatively (see Fig. 2b) while the butyltins were recovered with 10 ml 50% CH_2Cl_2 in *n*-hexane yielding recoveries of more than 80%, but no phenyltins were eluted (see Fig. 1).

Another application of argentation chromatography is the separation of unsaturated compounds such as lipids which is based on the ability of unsaturated organic compounds to form charge–transfer complexes with transition metals. Stability

studies of these complexes showed that unsaturated acyclic and carbocyclic compounds form more stable complexes than aromatics do [27]. Therefore, we tried to elute the phenyltins by decreasing the interaction between the silver ions and the phenyltins by eluting with 5 ml toluene followed by 6 ml of 10% 1-octene in toluene but no phenyltins were recovered. The use of more polar eluents such as 50% methanol in CH_2Cl_2 or pure methanol only led to elution of $AgNO_3$ from the silica column.

Nevertheless argentation chromatography represents an effective method for the removal of organosulfur compounds which allows the determination of all butyltins without interferences.

3.3. In situ sulfur elimination in the vial

Since the clean-up with Al_2O_3 is an established method in OT analysis and the recovery of the OT compounds is very high (above 90%, see Fig. 1). We examined the removal of sulfur compounds directly in the vial after evaporating the first fraction of the sediment extract, chromatographed over Al_2O_3, to a volume of 1 ml. With activated copper only elemental sulfur was removed and losses of the phenyltins up to 50% occurred (see Fig. 1).

$AgNO_3$-coated silica gel removed all interfering sulfur compounds nearly quantitatively after 2 h (less then 1% remained in the extract) yielding recoveries of the butyltins from 85 to 92%. But, again, the phenyltins were lost completely (see Fig. 1). However, treatment with $AgNO_3$-coated silica gel has been found to be an easy and effective method for the elimination of all interfering sulfur compounds. Fig. 3b shows a chromatogram of the same sediment extract as in Fig. 3a after treating the solution with $AgNO_3$-coated silica gel directly in vial.

4. Conclusions

Up to now many clean-up procedures have been applied to OT analysis in order to separate organic contaminations and lipids, but their efficiency in eliminating organosulfur compounds is limited.

The proposed method using 25% $AgNO_3$-coated silica gel for chromatography or treatment directly in the vial offers an easy and effective way for the quantitation of butyltin compounds in sediment extracts with high sulfur content. Since no interference between pentylated phenyltins and organosulfur compounds occur, phenyltins can be quantified directly after the Al_2O_3 clean-up column. A small amount of $AgNO_3$-coated silica gel added directly into the vial eliminates organosulfur compounds which interfere with the butyltins and quantitation of the butyltins is possible.

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