Removal of sulfur interfering in the analysis of organochlorines by GC-ECD

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Elemental sulfur is frequently formed by microbial activities in terrestrial and aquatic systems under anoxic conditions. This is indicated with high sensitivity by the electron capture detector (ECD) and can render determining higher boiling organochlorines by gas chromatography using an ECD impossible. Three methods for removing sulfur were compared: treatment with copper powder, metallic mercury and tetrabutylammonium sulfite. The preparation of pyrogenic copper powder as described in the literature is unnecessary. We recommend that desulfurizing be performed with ultrasound treatment using commercially available copper powder without any pretreatment.

Introduction

Interference by elemental sulfur often appears in the gas chromatographic determination of organochlorines in soil samples from the ground water range, in sediments and digested sludges with electron capture detection. The sulfur originates under anaerobic conditions from microbial sulfate reduction (*via* sulfide) and the degradation of organic sulfur compounds. The sulfur content of sediments reaches concentrations of up to 2%.[1,2] Moreover, elemental sulfur is frequently applied in agriculture as a fungicide. Because high-chlorinated compounds are degraded by microorganisms mainly (or even exclusively) under anaerobic conditions, the presence of sulfur must be expected during relevant experiments.

Sulfur exists in the solid, liquid and gas phases in several states. Above boiling point S_8 molecules appear first of all, which decompose to lower aggregates ($\rightarrow S_6 \rightarrow S_4 \rightarrow S_2$) as the vapour temperature increases. We mostly find three peaks in the gas chromatogram.

Overlapping by sulfur peaks occurs in the retention range of penta- and hexachlorobenzene, hexachlorocyclohexanes (HCHs), dichlorodiphenylchloroethanes/ethenes (DDX compounds) and aldrin. If the sulfur content is clearly higher than the concentration of these polychlorinated organics, the electron capture detector (ECD) often becomes saturated for some time. Compounds with only one or two chlorine atoms eluating in the sulfur range give a much lower signal and the chances of determining these in the presence of sulfur are low.

Treatment with pyrogenic copper powder,[3,4] metallic mercury[5,6] or silver on silica gel,[7] and conversion with tetrabutylammonium (TBA) sulfite to thiosulfate[8] or with polymeric triphenylphosphine (TPP) to the corresponding sulfide,[9] are recommended for the removal of elemental sulfur in extracts. However, commercial polymeric TPP must be purified by long-term extraction with two extractants before use,[9] while the preparation of pyrogenic copper powder (Raney-copper) and silver-loaded silica gel is also laborious. There are other methods to convert elemental sulfur,[10,11] but the rigorous reaction conditions also change or destroy the organochlorines. In this paper three methods of treatment using both specially-prepared and commercially available copper powder, mercury and TBA sulfite are compared, and a recommendation is given.

Experimental

Apparatus

We used a Shimadzu (Tokyo, Japan) GC 14A gas chromatograph equipped with a J&W Scientific DB5 fused-silica capillary column (30 m × 0.25 mm id, film thickness 0.25 μm; Folsom, USA) and a Shimadzu ECD cell 9A (^{63}Ni). The conditions for the separation of organochlorines were: carrier gas N_2, 1.0 ml min^{-1}, split 1:50, injector and detector temperature 250 and 280 °C, respectively. The temperature was programmed from 60 to 250 °C at 6 °C min^{-1} with a final time of 10 min. We injected 1 μl of the solutions.

Reagents and chemicals

The reactive copper powder was prepared as prescribed in DIN 38407, part 2, p. 49, starting from a solution of copper sulfate. The powder should be stored under *n*-hexane in a nitrogen atmosphere at 4 °C. TBA sulfite reagent:[8] 3.39 g TBA hydrogen sulfate (Merck, Darmstadt, Germany) is dissolved in 100 ml water. The solution is extracted twice with 20 ml of *n*-hexane to remove any impurities. The solution is then saturated with 25 g of sodium sulfite. All chemicals used were of analytical grade.

The toluene solution for the recovery test contained the following components: penta- and hexachlorobenzene (PeCB and HCB), α-, β-, γ- and δ-hexachlorocyclohexane (HCH), 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD). The substances were purchased from Promochem (Wesel, Germany). *n*-Hexane, *n*-heptane or isooctane make suitable alternative solvents or extractants for the analysis of heavily volatile organochlorines. Customary copper powder < 63 μm was obtained from Merck. A solution of 580 μg sulfur per ml toluene was used to determine the capacity of desulfurizing agents.

Desulfurizing procedures

With copper powder: About 120 mg powder (a spatula tip corresponds to 120 ± 10 mg) is added to 2 ml of the extract in

a tightly sealed vial. The mixture is sonicated in a water bath for 10 min. The supernatant of the quickly precipitating powder can be immediately analysed; a centrifugation is not necessary.

With TBA sulfite (after Jensen *et al.*[8]): 2 ml of the extract is shaken for 5 min with 1 ml propan-2-ol and 1 ml TBA reagent. If the sodium sulfite precipitated disappears, more substance must be added in 100 mg portions until after repeated shaking solid material remains. 5 ml of water is then added, the test tube is shaken for another minute, and the phases are separated. The toluene phase can be injected in the gas chromatograph without any drying. With mercury: A relatively large mercury pearl (80–100 μl = 1.0–1.35 g) is added to 2 ml extract using a glass pipette. The extract is sonicated for 20 min in a water bath.

Results and discussion

Detection of sulfur by the ECD

The chromatograms of two sulfur solutions with different concentrations are given in Fig. 1. At concentrations below 2 μg ml^{-1} three peaks occur at 23.6; 29.5 and 34.0 min. The most intensive peak (retention time: 34.0 min) can probably be attributed to the S_8 molecule. The detector signal only correlates with the concentration at values <2 μg ml^{-1}. The response increases at higher concentrations exponentially and finally rapidly. This sharp increase is due to overloading or saturation of the ECD. This happens for the main peak at a concentration of about 5 μg ml^{-1}. The maximum deflection continues for a considerable period of time (10 min and longer). At 50 μg sulfur ml^{-1} the detector reaches the maximum response already at the first sulfur peak. Such high concentrations are damaging to the ECD and should be avoided. Overloading requires subsequent regeneration over 1–2 h. The detection limit for sulfur with the technique used amounted to 50 ng ml^{-1}. The appearance of sulfur in the gas chromatogram and the detector response vary sharply depending on the ECD type, the separation column and the chromatographic conditions.

Sulfur binding capacity of the reagents

Copper powder. 2 ml of sulfur solution with 580 μg ml^{-1} was treated with 1, 2 and 3 spatula points of copper powder. It turned out that one spatula of powder (120 mg) is sufficient to bind 99.2% of the sulfur present (1160 μg). The residual concentration was 4 μg ml^{-1}.

The copper powder, which during preparation is initially an intense red, changes colour after brief storage to reddish-brown and then dark brown. We observed no pyrogenic properties even for a relatively fresh product (one day after preparation). These are evidently lost very quickly, which does not, however, influence the sulfur binding capacity. When stored as mentioned above, the powder's reactivity to sulfur remained unchanged even after 3 months. Attempts were also carried out with purchasable copper powder without any pretreatment. The sulfur content was lowered when applying 150 mg powder and a reaction time of 10 min to 42%. The addition of more powder had no effect. However, prolonging the treatment to 20 min reduced the sulfur content to less than 3% of the original concentration. Consequently purchasable copper powder can be used and the expensive preparation of special powder is unnecessary. We also tested the suitability of zinc powder, but there was no reaction.

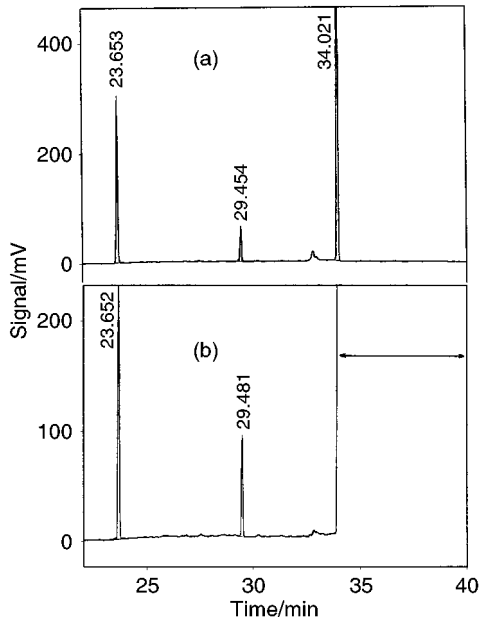

Fig. 1 Gas chromatograms of sulfur solutions, (a) 1.16 μg ml^{-1}, (b) 5.80 μg ml^{-1}.

TBA sulfite. 2 ml of sulfur solution (580 μg ml^{-1}) was desulfurized quantitatively with 1 ml reagent. The supplementary addition of sodium sulfite was necessary.

Metallic mercury. Initially we sonicated the sulfur solution with the mercury for 10 min. In this way 32% of the sulfur in the solution could be removed. The increase of the reaction time to 20 min allowed the sulfur to be removed down to residues of 1–3%. Shaking on a machine for one hour, even at high intensity, had a much lower efficacy. A disadvantage of the method is the use of toxic mercury.

Recovery

It is to be expected that copper powder functions as an adsorbent. We carried out recovery determinations using a test solution of organochlorines in order to check the adsorption effect. The results are given in Table 1.

The powder added was *n*-hexane-humid because of its storage in *n*-hexane. Dilution by the hexane (determined at 0.048 ml per spatula of powder) was taken into consideration arithmetically. The internal standard used for quantification (4-chlorobenzotrichloride) was added with the dilution after treatment with the powder. The values in Table 1 show the significant adsorption of the substances. Four spatulas of powder were used only in order to demonstrate the effect; such a quantity is not necessary.

The amount of adsorbed substance increases proportionally to the concentration in the solution in accordance with the

Table 1 Recovery values for different quantities of copper powder specially prepared (S.T. = spatula tip)

	Concentration/ μg ml^{-1}	Recovery (%)		
		1 S.T.	2 S.T.	4 S.T.
PeCB	15.61	82.3	64.0	54.2
α-HCH	22.28	82.2	67.5	57.9
HCB	15.17	81.7	65.4	53.0
β-HCH	17.15	80.2	62.1	50.4
γ-HCH	23.55	81.5	65.5	56.6
δ-HCH	16.47	79.6	62.8	51.3
DDE	35.76	76.7	61.5	50.3
DDD	41.08	81.1	60.3	47.9
DDT	50.42	81.9	67.7	52.2
Average recovery	./.	80.8	64.1	52.6

equations of Langmuir and Freundlich. Consequently the effect is lower at small concentrations. At 1/100 of the concentrations quoted in Table 1, *i.e.* the range 150–500 ng ml^{-1}, the mean recoveries amounted to 99, 97 and 90% for 1, 2 and 4 spatula(s) of copper powder, respectively. Therefore adsorption losses of organochlorines can be neglected if concentrations are < 1 $\mu g\ ml^{-1}$.

The mean recovery value using the concentrations of Table 1 and one spatula of common (purchasable) powder amounted to 96.8% (20 min treatment) compared with 80.8% for the pyrogenic powder. The large difference between the two powders was confirmed by repeated experiments. Even after a storage time of 5 months the mean recovery for the prepared powder only increased from 80.8 to 82.1%. The lower adsorption capacity (with the consequence of better recovery values) of the purchasable powder in comparison to the freshly prepared one is evidently caused by the different size and nature of the particles. We found no losses of organochlorines in the removal of sulfur by the TBA sulfite method or by treatment with metallic mercury.

Fig. 2 shows the chromatograms of the toluene extract from sediment of the Spittelwasser stream (near Bitterfeld, Saxony-Anhalt) before and after treatment with commercially available copper powder. In the untreated extract, the DDX compounds cannot be determined.

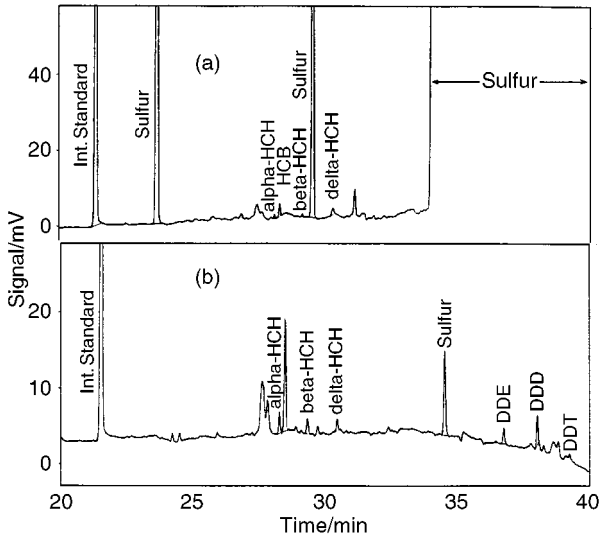

Fig. 2 Gas chromatograms of the extract from a sediment sample, (a) original, (b) after desulfurization with commercially available copper powder.

Conclusion

As the result of our experiments we recommend the removal of interfering sulfur in extracts by ultrasound treatment with purchasable, common copper powder. This is sufficiently reactive to sulfur, but requires a somewhat longer reaction time. The preparation of pyrogenic powder is not necessary. The binding of sulfur with tetrabutylammonium sulfite after Jensen *et al.*[8] is also a simple and safe method.

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