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An advantageous reagent for the removal of elemental sulfur from environmental samples

Jan T. Andersson, Ulrich Holwitt

Abteilung für Analytische Chemie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 8, D-48149 Münster, Germany

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Abstract. Polymeric triphenylphosphine is introduced as an efficient reagent for the removal of elemental sulfur from environmental samples. It is compared with several traditional reagents, particularly heavy metals. For all reagents, ultrasonication was much preferable to stirring or shaking the reaction solution. Advantages of the new reagent include quantitative reaction with sulfur, few side-reactions with analytes, ease of handling and non-hazardous products. The used reagent can be regenerated and reused.

1 Introduction

Elemental sulfur frequently interferes with the determination of environmentally relevant compounds, particularly in samples such as sediments and sewage sludges. Being a link in the sulfur cycle, it is formed in large amounts via sulfate-reducing bacteria which produce sulfide. This can be oxidized by sulfide-oxidizing bacteria or chemically by e.g. oxygen. It can reach levels of 1% or more (dry weight) in samples like a non-pristine coal [1] or harbor sediments (e.g. Standard Reference Material 1941 [2] or some recently investigated sediments from Rotterdam Harbor (1.5% sulfur) or Venice (up to 2.5% sulfur) [3]). It has furthermore been found in matrices as diverse as lichen and air [4]. In such cases it can by far dominate many environmentally important organic compounds and be a major interference. Since elemental sulfur in many respects behaves as an organic molecule, it is extractable with most organic solvents used in sample preparation and it can easily be chromatographed in the gas as well as the liquid phase. The dominating form at room temperature are S_8 rings but under catalytic conditions or at slightly elevated temperatures (as found in a standard split-splitless-injector), a dynamic allotropic equilibrium

$$S_6 \rightleftharpoons S_7 \rightleftharpoons S_8 \ \ldots$$

insures that sulfur does not elute from gas-chromatographic columns as a single peak; in fact, quite a complex chromatogram is obtained from the pure element (Fig. 1a). On stationary phases of low polarity (e.g. 5% phenylmethylsiloxane), the sulfur S_8 peak alone can obscure the whole region from ca. 1700 to 1900 retention index units [5] and makes the determination of many compounds impossible.

A large number of reagents have been suggested for the removal of sulfur, and several of them are commonly used in analytical work-up schemes. In Table 1, some of the more important reagents are listed together with the reaction products and relevant references. Most of them are based on the use of heavy metals. This is a ground for objection to their use, since heavy metals are toxic in

Table 1. Commonly used desulfurization reagents and their reaction products

Desulfurizing agent	Reaction product	Reference
Silver on silica gel ("Ag/SiO$_2$")	Ag_2S	[5]
Copper powder ("Cu")	CuS	[6]
Mercury ("Hg")	HgS	[7]
Copper amalgam ("Cu/Hg")	CuS/HgS	[8]
Tetrabutylammonium sulfite ("TBAS")	$(TBA)_2S_2O_3$	[9]
Polymeric triphenylphosphine ("TPP")	Polymeric $Ph_3P=S$	[8]
Potassium hydroxide	S_n^{2-}	[10]
Superactive alumina (as column filling)		[11]
Distilled water (ultrasonicating)		[12]
Raney-nickel	NiS	[13]
Raney-copper	CuS	[14]
Silver nitrate on silica gel	Ag_2S	[15]

Dedicated to Professor Dr. Dieter Klockow on the occasion of his 60th birthday

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Correspondence to: J. T. Andersson

many instances and severe pollutants, and their use should be discouraged as far as possible, also in the analytical laboratory. We therefore decided to look for an alternative which should fulfil as many as possible of the following criteria:

1. Quantitative removal of elemental sulfur under mild conditions
2. No side reactions with common analytes
3. Low toxic and pollution potential
4. Convenience (easy handling, fast reaction, easy separation from reaction mixture, low cost).

We decided to look at organic reagents in order to avoid heavy metals and settled for triphenylphosphine. The reaction of this compound with sulfur gives triphenylphosphine sulfide and was first described in 1881 [16]. The use of the (commercially available) polymeric triphenylphosphine should simplify the removal of unused reagent and product. The monomeric phosphine probably reacts faster than the polymeric but work-up becomes more laborous, excess triphenylphosphine and its reaction products, the sulfide and possibly the oxide, must be removed. A column-chromatographic removal is conceivable but may be difficult to achieve due to the relatively large polarity range of those compounds which might lead to severe losses of the analytes. Since the sulfide can easily be reduced to the phosphine, the reagent is also recyclable [17].

In this work we investigate the conditions for complete removal of elemental sulfur with polymer-bound triphenylphosphine (TPP), try to estimate the extent of side reactions with pesticides and sulfur-containing analytes, check the performance with a real-world sample and compare the reagent throughout with several traditional desulfurizing reagents, namely silver on silica gel, tetrabutylammonium sulfite, mercury, copper and copper amalgam. We do not aim at a presentation of a fully developed method but want to draw attention to the possibilities offered by this new reagent in comparison with customary reagents.

2 Experimental

2.1 Reagents and apparatus

All solvents were Nanograde (Promochem, Wesel, Germany). The pesticides and sulfur-containing analytes were dissolved in toluene at ca. 50 µg/mL and sulfur at 800 µg/mL. The polymeric triphenylphosphine (3 mmol/g) was purchased from Fluka (Neu-Ulm, Germany). Gaschromatographic determinations were performed on a HP 5890 II equipped with a split-splitless-inlet (250 °C) and the atomic emission detector 5921 A (AED). The column was 25 m, i. d. 0.32 mm, film thickness 0.17 µm HP-1. The temperature program in the figures was 60 °C for 2 min, 5 °C/min to 300 °C, hold for 5 min. Generally 1 µL was injected.

2.2 Purification of TPP

The polymer was extracted for 48 h with dichloromethane (200 mL) followed by toluene (200 mL) for 48 h in a Soxhlet apparatus (100 mL volume). The polymer cleaned in this way was perfectly satisfactory for the present purposes and further extraction did not produce a cleaner polymer. The reagent was stored in toluene in a closed brown bottle. Before use, the required amount was removed from the bottle, large particles crushed and rinsed with approximately 1 mL of toluene.

2.3 Desulfurizations

Each experiment was carried out twice, and each GC determination was done in duplicate. The data in Tables 2 and 3 are the mean values of these four determinations together with the standard deviation. The external standard for the sulfur AED response was prepared from the standard solution (800 ng/µL) of recrystallized sulfur (toluene) in toluene.

2.3.1 With TPP. The polymer was dried in a gentle stream of nitrogen, weighed and added to the solution to be desulfurized. After the reaction in the ultrasonic bath (a

Table 2. Recovery [%] of pesticides and sulfur after desulfurization with selected reagents

	Ag/SiO_2	Cu/Hg	TPP	Cu	TBAS	Hg
Dichlorvos	86 ± 7	99 ± 11	56 ± 14	88 ± 10	71 ± 13	94 ± 22
Nicotine	8.2 ± 2.6	44 ± 22	105 ± 11	29 ± 14	122 ± 11	65 ± 53
Phoxim	58 ± 18	72 ± 21	82 ± 17	72 ± 13	83 ± 14	94 ± 25
Fenuron	0.7 ± 0.1	104 ± 13	93 ± 10	90 ± 9	96 ± 77	94 ± 21
Methabenzthiazuron	27 ± 2	104 ± 13	92 ± 9	89 ± 10	109 ± 28	93 ± 25
Atrazine	22 ± 3	95 ± 11	96 ± 5	88 ± 10	96 ± 13	94 ± 23
Metribuzine	20 ± 4	98 ± 12	98 ± 3	90 ± 8	98 ± 8	89 ± 21
Aldrin	103 ± 6	102 ± 10	100 ± 5	89 ± 8	98 ± 9	92 ± 21
Isodrin	97 ± 5	101 ± 10	100 ± 4	89 ± 8	99 ± 9	92 ± 21
Allethrin	41 ± 2	102 ± 10	105 ± 3	91 ± 7	99 ± 35	92 ± 22
DDE	97 ± 4	102 ± 9	104 ± 9	91 ± 8	98 ± 9	89 ± 24
Endrin	98 ± 4	102 ± 10	101 ± 3	90 ± 8	99 ± 9	95 ± 20
DDT	95 ± 5	101 ± 10	88 ± 22	91 ± 7	98 ± 11	93 ± 21
Cypermethrin	91 ± 5	103 ± 11	92 ± 7	94 ± 9	104 ± 14	94 ± 23
Sulfur	n.d.[a]	0.11	n.d.[a]	<0.1	<0.1	n.d.[a]

[a] n.d. = not detected

Table 3. Recovery of sulfur-containing test compounds and sulfur after desulfurization with an excess of reagent

	Ag/SiO_2	Cu/Hg	TPP	Cu	TBAS	Hg
BTC	n.d.	93 ± 3	86 ± 1	102 ± 9	9.1 ± 0.5	48 ± 9
TN	n.d.	76 ± 7	101 ± 16	86 ± 3	106 ± 26	30 ± 13
ETos	81 ± 13	95 ± 6	92 ± 1	91 ± 3	87 ± 16	92 ± 9
DPS	93 ± 12	98 ± 6	91 ± 3	94 ± 4	88 ± 15	92 ± 8
DBT	96 ± 11	99 ± 6	93 ± 2	95 ± 4	89 ± 14	92 ± 8
TDS	4.4 ± 0.2	97 ± 5	95 ± 2	95 ± 2	89 ± 17	92 ± 9
$DBTO_2$	76 ± 12	83 ± 11	95 ± 7	56 ± 14	38 ± 4	107 ± 20
XAS	14 ± 1	101 ± 8	100 ± 13	97 ± 1	81 ± 20	110 ± 8
SMS	48 ± 7	99 ± 6	96 ± 3	97 ± 2	92 ± 15	95 ± 4
Sulfur	n.d.[a]	79 ± 8	n.d.[a]	67 ± 7	n.d.[a]	n.d.[a]

[a] n.d. = not detected

conventional laboratory cleaner, 60 W) the reagent was filtered off and the filtrate was concentrated in a nitrogen stream to a final volume of 1 mL in a conical 5 mL flask.

2.3.2 Silver on silica gel. The preparation was performed according to Ref. [5] and the reagent stored in the dark. Initial experiments were performed in the column mode with a weighed amount of reagent added to toluene in the column. After addition of the reaction solution, the desired reaction time could be attained by stopping the flow. Elution was done by adding more toluene. For the test solutions, 50 μL sulfur-containing solution was added and the elution took place with 5 mL of toluene. When ultrasonication was used as reaction mode, the solution to be desulfurized was diluted with 2 mL of toluene in a 10 mL flask, the reagent added and the flask stoppered and placed in the ultrasonic bath. After the reaction the reagent was filtered off through a glass frit and washed with 3 mL toluene. The volume of the solvent was reduced as above.

2.3.3 Copper. Before the reaction, the copper powder was washed with 2 mL of conc. HCl to remove dark red Cu_2O, then under an atmosphere of N_2 with distilled water (3×2 mL), methanol (3×2 mL) and toluene (2×2 mL), before it was rinsed into the reaction flask with a 2 mL portion of toluene. The reaction conditions were the same as for silver on silica gel. After the desulfurization, the copper powder was filtered off and washed with toluene.

2.3.4 Mercury and copper amalgam. The reaction conditions were the same as for silver. After the desulfurization, the reagent was filtered off and washed with toluene.

2.3.5 Tetrabutylammonium sulfite. The reagent was an aqueous solution of sodium sulfite (2 mol/L) and tetrabutylammonium hydrogen sulfate (50 mmol/L). The desired amount was shaken with the sulfur-containing solution, 2 mL toluene and 1 mL of either methanol or isopropanol. After a reaction time of 5 or 2 min (shaking or ultrasonication, resp.), 2 mL of water were added and the phases separated. The aqueous phase was washed three times with 0.5 mL toluene which was then dried with $MgSO_4$.

2.4 Sewage sludge

The sludge was collected at the municipal sewage sludge treatment plant at Münster-Coerde. It was air dried for four days. A 3 g portion of the dried material was ground, mixed with 1 g sodium sulfate and Soxhlet extracted for 24 h with toluene (170 mL). The volume was reduced to ca. 10 mL under reduced pressure and to 2 mL with a stream of nitrogen. The solution was chromatographed on silica (70–230 mesh) and eluted with 50 mL of a toluene-methanol (4:1) mixture. The volume was again reduced to 2 mL and treated with 40 mg TPP for 2 h in the ultrasonic bath.

2.5 Reduction of spent TPP

1.13 g (~3.3 mmol) used triphenylphosphine are added to a suspension of 2.3 g (0.1 mol) Na in toluene, then refluxed and stirred with a Herschberg-stirrer for 12 h. The polymer was filtered off, the lumps of remaining Na picked up with a tweezer and the smaller pieces destroyed by washing the filter with isopropanol. Finally, the polymer was washed with small portions of toluene. It was cleaned in a Soxhlet apparatus as above before renewed use.

3 Results

Commercial polymeric triphenylphosphine (TPP) must be purified before use since it gives off a large number of compounds on extraction with organic solvents. Those compounds appear in the gas chromatogram and can easily obscure any analytes. Exhaustive extraction with dichloromethane followed by toluene in a Soxhlet apparatus was found to be satisfactory. Large batches can be prepared at once and can be stored in toluene until needed.

To obtain easily reproducable reaction conditions, toluene was selected as solvent because of its excellent solubility for sulfur, its low vapor pressure (to exclude concentration effects), as a commonly used solvent for environmental samples, and, most importantly, as a solvent that wets the polymeric TPP, in contrast to aliphatic solvents.

In order to establish the most useful reaction conditions, a solution of sulfur in toluene was allowed to react with different amounts of TPP and for different lengths of time. The solution with the suspended polymer was stirred in the first experiments but ultrasonication proved to be much superior (shorter reaction times, less reagent needed, more reproducible results) and was used subsequently for all the other reagents, too. The sulfur remaining after the reaction was quantified using gas chromatography with an atomic emission detector (AED) for sulfur-selective detection.

The time and amount of the different reagents needed to effect complete sulfur removal under standardized conditions (40 µg of sulfur in 2 mL of toluene, ultrasonication at ca. 45 °C, other desulfurizations at room temperature) are shown in Table 4. It is obvious that a considerable reduction in both reaction time and amount of reagent can be achieved using ultrasound compared to the conventional column, stirring or shaking procedures. Furthermore, the reproducibility was markedly better with ultrasound. Tetrabutylammonium sulfite was the most difficult reagent to use because of the time needed to achieve a complete phase separation and because of the occasional formation of a precipitate of sodium sulfite which had to be filtered off and washed separately. It is also the more time-consuming method, needing about twice the preparation and work-up time of the other methods.

In analytical desulfurizations an excess of reagent is necessary since it is not known beforhand how much sulfur is present in the sample. An important parameter to investigate is therefore the reactivity of the reagents towards the analytes of interest. Ideally this should be assessed in each case for the analytes under investigation before any desulfurizing agent is used. Here we made an exploratory study for the several reagents using fourteen pesticides and nine organosulfur compounds as representatives of very commonly investigated environmental chemicals and of compounds which may show reactivities towards the desulfurzing agents similar to those of elemental sulfur.

3.1 *Pesticide analytes*

The pesticides were chosen to represent a wide variety of chemical classes, including chlorinated and non-chlorinated ones. A solution containing 5 µg of each pesticide and 40 µg of sulfur in toluene was treated with the desulfurization reagents under the conditions shown leading to a quantitative desulfurization for each reagent with a pure sulfur solution (cf. Table 4). The effects of prolonged reaction times with excess reagent were also investigated. Controls (no sulfur, no reagent) were run to correct for possible breakdown reactions or losses of analyte.

All six reagents showed excellent reactivity towards sulfur; only in the case of copper amalgam was a trace of sulfur (0.1% of initial content) left even in the presence of excess reagent. Except for mercury and TPP, in the presence of pesticides the reagents had to be used in excess of the amounts calculated on basis of the results in Table 4, otherwise significant amounts of sulfur remained. The recovery of the pesticides (corrected for losses as determined in the control runs) depended to some degree on the reagent (Table 2). Silver on silica led to poor recovery for most of the analytes but in the other cases only dichlorvos, phoxim and nicotine varied appreciably between the reagents. Dichlorvos and phoxim are esters of phosphoric and thiophosphoric acid, respectively, and might be hydrolytically unstable. Nicotine was problematic in four out of the six cases. Another factor might be that those compounds are the most volatile ones of the pesticides tested and that their losses might therefore be more difficult to reproduce.

The control recoveries (in the absence of sulfur) were good except for silver on silica; here about 30% of the analytes were lost. TPP and copper amalgam showed the best results. The reproducibility in recovery in the parallel runs differed a lot, silver, mercury and the TBA sulfite reagent showing relatively poor results, the latter one presumably because of the need for an aqueous phase for this reaction.

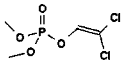
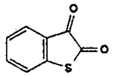
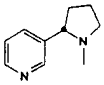
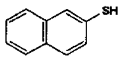
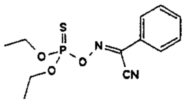
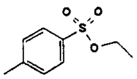
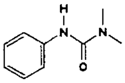
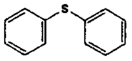
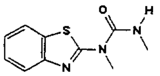
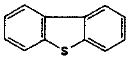
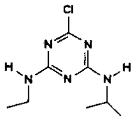
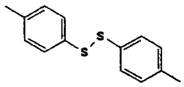
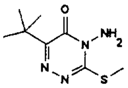
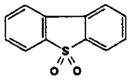
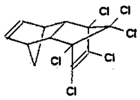
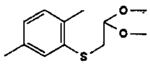
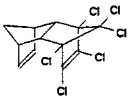
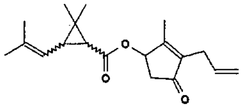
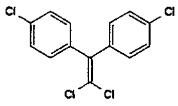
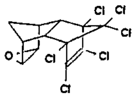
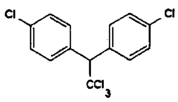
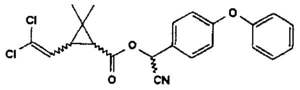
3.2 *Sulfur-containing analytes*

Since the reagents are designed to react with sulfur, it is appropriate to check their behavior toward sulfur-containing analytes also. Sulfur is part of many environmentally relevant compounds, e.g. certain triazine herbicides, polycyclic aromatic sulfur heterocycles and thiophos-

Table 4. Conditions for the complete removal of 40 µg sulfur from a pure solution of sulfur in toluene

Desulfurization reagent	Mode	m [mg] or V [mL]	Reaction time [min]	Time needed for prepn. and work-up [min]
Silver on silica gel	stir	133 mg	180	120
	ultrasonication	75 mg	60	120
	column	50 mg	180	180
Copper amalgam	stir	8 mg	60	120
	ultrasonication	2 mg	5	120
Polymeric TPP	stir	ca. 25 mg	ca. 1000 (1 d)	140
	ultrasonication	25 mg	120	140
Copper powder	ultrasonication	2.5 mg	10	140
TBAS, 1 ml MeOH	ultrasonication	0.5 mL	15	330
TBAS, 1 ml ^{i}PrOH	shake	1 mL	5	300
TBAS, 1 ml ^{i}PrOH	ultrasonication	0.1 mL	2	300
Mercury	stir	25 mg	900	120
	ultrasonication	15 mg	20	120

Table 5. Pesticide and sulfur-containing test compounds

Pesticide	Formula	Sulfur-containing substance	Formula
Dichlorvos		Benzo[b]thiophene-2,3-quinone (BTC)	
Nicotine		β-Thionaphthol (TN)	
Phoxim		Ethyl p-toluene sulfonate (ETos)	
Fenuron		Diphenyl sulfide (DPS)	
Methabenz-thiazuron		Dibenzothiophene (DBT)	
Atrazine		bis-(4-Methylphenyl) disulfide (TDS)	
Metribuzine		Dibenzothiophene sulfone (DBTO$_2$)	
Aldrin		(2,5-Dimethylphenyl) 2,2-dimethoxy-1-ethyl sulfide (XAS)	
Isodrin		Stearyl methyl sulfide (SMS)	
Allethrin			
DDE			
Endrin			
DDT			
Cypermethrin			

phoric esters. Nine compounds were selected to represent reduced as well as oxidized sulfur functionalities (Table 5).

Silver on silica gel was more destructive than the other reagents for this group of compounds, too (Table 3). As could be expected, β-thionaphthol was the most sensitive analyte and reacted to a considerable extent with all the metallic reagents. The large variations in recovery for this compound can also result from the air sensitivity of the thiol group. The loss of benzothiophene quinone, a product of photochemical [18] and microbial metabolic [19] oxidation of benzothiophene, with the TBA sulfite reagent can be explained by the hydrolysis of the quinone ring in aqueous solvent [18] whereas the appreciable losses of dibenzothiophene sulfone with three of the reagents are more difficult to rationalize. Surprisingly, copper and copper amalgam showed poor sulfur removal efficiency in those experiments, also in cases when they were added in fourfold amount over what was necessary to effect complete desulfurization in the absence of analytes or with the pesticides. Since the sulfur-containing analytes can be removed from the copper by simple rinsing with toluene, it is not likely that they adsorb strongly enough on the metal surface to block the reaction with elemental sulfur.

The experience with the two groups of compounds led to the following characterization of the six desulfurizing reagents. Silver on silica gel has to be used in excess in order to effect complete desulfurization but, at the same time, shows a high reactivity towards many sample components, probably a result of the high activity of the fine silver particles on the silica surface. Copper shows a much lower reactivity towards sample components but even used in excess it does not seem to lead to complete removal of sulfur. Too large an excess is, on the other hand, undesirable since this ultimately might facilitate side reactions with sensitive analytes. The same characteristics apply to copper amalgam. Use of the last metal investigated, mercury, led to poor reproducibility of analyte recovery, possibly as a result of irreproducible generation of mercury droplets in the ultrasonic bath, but sulfur was efficiently captured.

Tetrabutylammonium sulfite cannot be recommended for use with water-soluble analytes; a significant problem is their loss through extraction into the aqueous medium. Moreover, side reactions such as bisulfite addition or reduction of suitably substituted analytes are conceivable and may lead to an additional loss of analyte.

Polymeric TPP caused quantitative removal of sulfur under easily reproducible conditions. It needs a fairly long reaction time (on the order of 2 h) and extensive batch purification before use, but those drawbacks were offset in our experiments by the fact that side-reactions of the analytes were negligible, also under conditions of prolonged reaction times and excess reagent.

3.3 Sewage sludge

In order to gain some experience with the new reagent in more complex situations, a sewage sludge sample was selected for a desulfurization experiment. This investigation was supposed to demonstrate the desulfurization potential of polymeric TPP even in the challenging case of an environmental sample. Comparative reagents in this case were tetrabutylammonium sulfite and copper, which were chosen from the previously used ones to represent one heavy metal reagent and a commonly used liquid heterogeneous system. The worked-up sludge had a low sulfur content, ca. 1 mg/g (dry weight). Since copper caused less than complete removal of sulfur in the test situations above, it was used in a twentyfold excess here. The sulfur-selective traces of the sample before and after treatment with the three reagents are shown in Fig. 1. The chromatogram in Fig. 1a shows essentially the typical multipeak appearance of sulfur which is repeated, albeit at lower intensity, after the reaction with copper powder (Fig. 1b). TPP and tetrabutylammonium sulfite removed sulfur completely (Fig. 1c, d). The GC traces in the latter two cases display several small peaks which do not seem to be present in the sample, e.g. at a retention time of 39 min. They are not present in the control runs (compare also Fig. 1b); on the other hand, it is difficult to understand why they appear in solutions with such different reagents as TPP and the TBA sulfite. It must be stressed, however, that those changes are only seen close to the detection limit.

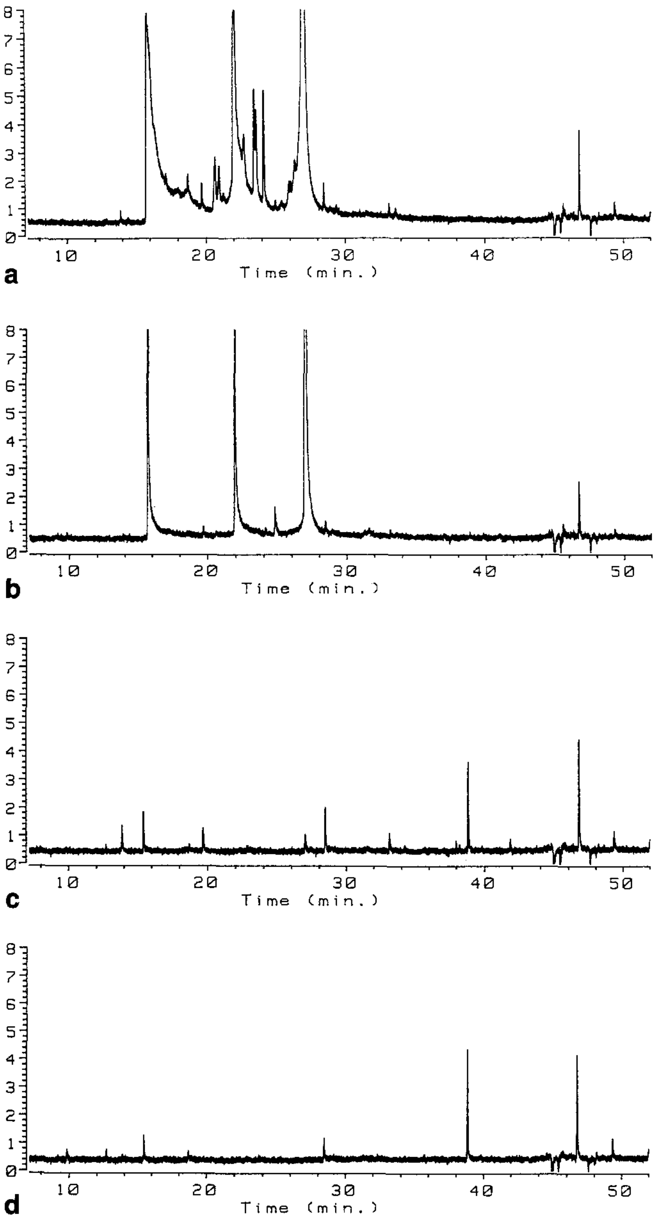


Fig. 1a–d. S-selective traces of gas chromatograms of sewage sludge: **a** before desulfurization, **b** after desulfurization with copper powder, **c** after desulfurization with TPP, **d** after desulfurization with TBAS (^{i}PrOH)

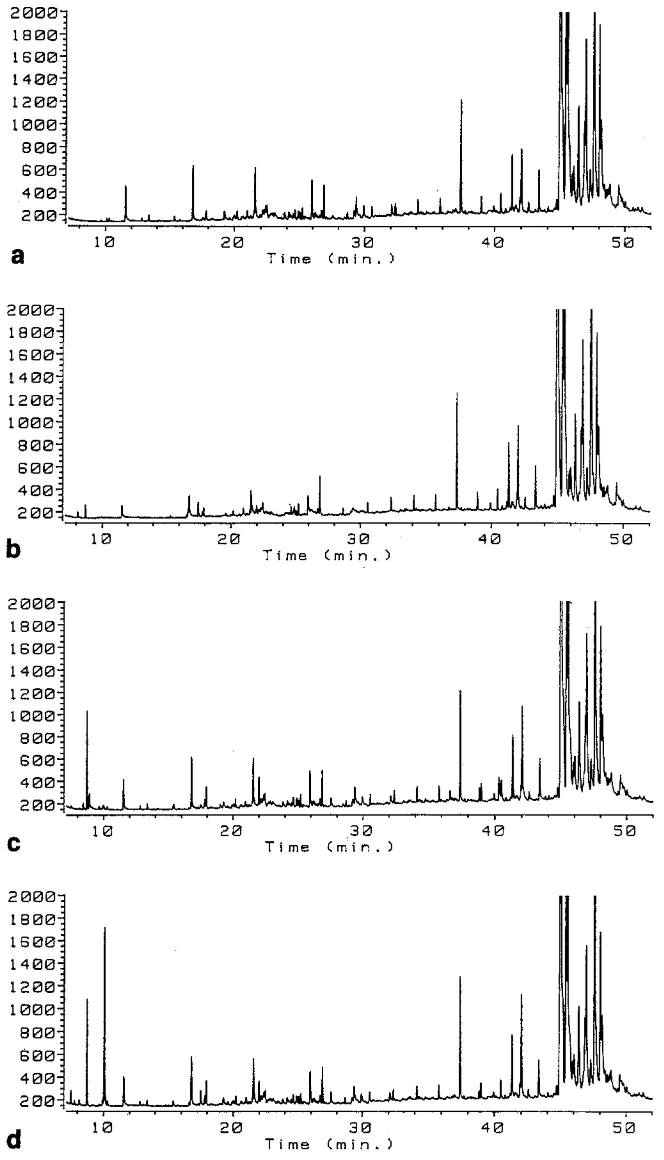


Fig. 2a–d. C-selective traces of gas chromatograms of sewage sludge: **a** before desulfurization, **b** after desulfurization with copper powder, **c** after desulfurization with TPP, **d** after desulfurization with TBAS (^{i}PrOH)

The carbon-selective traces are displayed in Fig. 2 and reveal that all reagents slightly alter the pattern of the sludge components. With TPP and, in particular, the TBA sulfite, two peaks appear at the beginning of the chromatogram (at 8.8 and 10 min), whereas with copper several of the smaller GC peaks are reduced in size (in the Figure, the peak heights before and after desulfurization should be comparable). No attempt was made on identifying the peaks since our interest was centered on the desulfurization properties of the polymeric phosphine.

3.4 Reduction of used TPP

The triphenylphosphine polymer reacts with sulfur to the sulfide. Since triphenylphosphine sulfide can easily be reduced in homogeneous solution to yield triphenylphosphine [17], it should be possible to reactivate spent TPP polymer for reuse. Indeed, reduction with Na led to a polymer which was less dark in color than the fresh polymer buth which possessed an IR-spectrum indistinguishable from that of the original polymer. A desulfurization of a sulfur solution in toluene proceeded as smoothly as with new reagent. Thus the polymer can easily be recycled if desired.

4 Conclusions

The comparison demonstrates that TPP is an excellent alternative to the traditional desulfurization agents. It leads to complete removal of sulfur although the reaction times necessary are somewhat longer than with heavy metals. The side reactions observed with several pesticides, sulfur-containing analytes and sewage sludge components are very modest and comparable to or less extensive than with other reagents. A drawback is the cleaning of the polymer which is unescapable with the commercial product, but if this is done with a large batch at one time, the time demanded by this step is less significant. The use of ultrasonic reaction conditions is highly beneficial. Unlike the heavy metal reagents, TPP does not produce any hazardous wastes and used reagent can be disposed of as a harmless organic substance. Alternatively, the spent reagent can be regenerated and used again.

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