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Observations of the Reaction between Organohalides and Sulfite

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■ The reactivity of aqueous sodium sulfite with 11 chlorinated compounds and total organic halogen content of seven water sources was studied to determine the effect of dechlorination on the quantitation of halogenated organics. Reaction rates were analyzed by the total organic halogen procedure (TOX) and by purge and trap gas chromatography (GC). Significant reductions of 3-bromopropene in the presence of sulfite were observed; reaction kinetics were highly pH dependent and modeled as pseudo first order. Slight reductions are observed for other compounds at short reaction times and room temperatures. Significant differences (>25%) were observed between TOX concentration of waters dechlorinated at acidic and basic conditions with sodium sulfite. Reactivity of sulfite ions with TOX appears to be dependent upon initial TOX concentrations, pH, and length of reaction time.

I. Introduction

Dechlorination of effluents released to the environment is necessary to reduce toxicity of free chlorine and chloramines. Recent evidence suggests that sulfites, used for dechlorination, may also react directly with chlorinated organics produced during disinfection to reduce mutagenicity (*1*, *2*). Wilox and Horth (*3*) conducted microbial assays on concentrated extracts of various surface waters subjected to both chlorination and industrial pollution. Samples from a water treatment facility, partially dechlorinated with sulfur dioxide (0.5 mg/L residual), were processed and assayed for mutagenic activity in parallel. The result confirmed that dechlorination attenuated mutagenic activity. Furthermore, water that had been completely dechlorinated proved slightly less mutagenic than the partially dechlorinated samples.

Recent studies have indicated that sodium sulfite, used to dechlorinate water samples prior to TOX analysis, is reactive with the halogenated compounds of interest. Sorrell noted a decline in TOX concentrations of stored surface water samples dechlorinated with sulfite and an increase in untreated samples (Sorrell in ref 4). Sorrell later determined that optimal storage conditions for dechlorinated samples required acidification with refrigeration. Decay of the samples was attributed to (possible) "decomposition of the metastable organohalides formed during the chlorination process." Stanbro and Lenkevich (*5*) demonstrated that several organic chloramines are not instantaneously reduced by aqueous sulfite ion, as had been previously assumed, and may require several hours to dechlorinate. Sulfite was reported to react with brominated dihaloacetonitriles (*6*). Fam and Stenstrom (*7*) observed significant reductions of pure compounds in the presence of sulfite. They also found that a significant portion of the nonvolatile GC chlorinated organics produced during chlorination of reclaimed waste water was attenuated or eliminated from solution by dechlorination prior to solvent extraction and GC analysis. However, the fraction of total organic halogen (from the chlorination of water and humic acid preparations) amenable to direct analysis by gas chromatography may range from 0.1% (*8*, *9*) to 50% (*10*). Thus, these initial observations only apply to a portion of chlorination byproducts.

The chemistry of dehalogenations is well documented. Reaction categories include 1,2-dehalogenations, substitutions, and eliminations (*11*, *12*). Dehalogenations are also promoted by electrochemical means, heating, and radiation. The range of reactivity and reported mechanisms is enormous and generally reported for solvents other than water. For many organohalogens, the tendency for halogen substituents to be attacked by ionic or radical reductants is I > Br > Cl > F; identical with the leaving group abilities of halogens in nucleophilic displacements (*11*, *13*). Important nucleophiles, potentially present in water, include organic and inorganic selenides, organometallic compounds, halide ions, sulfur and phosphorus nucleophiles, cyanide ions, amines, and hydroxide ions (*11*).

Schroeter's (*14*) review of sulfur dioxide reactions indicates that sulfites react with a variety of halogenated organics including alkanes, alkenes, carboxylic acids and esters, di- and trihalomethanes, and aryl and alkyl halides. Several classes of these compounds were identified as byproducts of the reaction between chlorine and aqueous humic substances or chlorinated water: halomethanes (*15*, *16*), haloacetic acids (*17*, *18*), chloral hydrate (*18*), and alkylene and aryl halides (*19*).

Any reaction between sulfites and halogenated organic molecules, whether directly with the carbon–halogen bonds or with other functional groups, may have significant implications with respect to chemical behavior, analysis, and toxicity. In this paper the effect of dechlorination with sulfites on the total organic halogen content of chlorinated water and the reaction of sulfites with selected pure compounds were investigated.

II. Experimental Section

All field samples were collected in annealed or acid dichromate washed glass bottles with Teflon-lined caps. Upon return to the laboratory, samples were dosed with additional chlorine (from calcium hypochlorite stocks) to a final residual between 1 and 2 mg/L (if necessary) to simulate conventional water treatment protocol and to prevent bacterial contamination. The DPD colorimetric method was used for analysis for total and free chlorine residual. Bottled distilled water was used for preparation of pure compounds and reagent blanks. All chemicals were reagent grade.

1. TOX Analysis. TOX analyses were conducted with both a Dohrmann AD-3 Adsorption Unit equipped with four dual carbon adsorption modules and an MC-3 Total Organic Halide Analyzer (Xertex Corp., Santa Clara, CA). The method is described in detail elsewhere (*20*). Blanks consisted of 100 mL of acidified distilled water. Reagent blanks included dechlorinating reagents and nitric acid. Calibration of the titration cell was conducted by direct injection of 5 μL of 200 mg/L (as Cl) sodium chloride stock solution (Dohrmann-Xertex, Sunnyvale, CA) prior to each set of analyses. Cell calibrations were within 5% accuracy. Replicate water samples were analyzed to verify that standard deviations were in the range associated with the method. Stock solutions of trichlorophenol were analyzed to verify accuracy and precision.

2. Purge And Trap Gas Chromatography. A Hewlett-Packard 5890A gas chromatograph equipped with electron capture detector and DB 624 (J&W Scientific)

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capillary column (30 m × 0.53 mm i.d.) was used. The instrument was coupled with a Tekmar LSC-2 purge and trap device (Tekmar, Cincinnati, OH). Conditions for the analyses were as follows: samples were purged with purified helium (40 mL/min) for 11 min at 30 °C with a subsequent desorption/bake step at 180 °C for 11 min. The GC was automatically started by the LSC-2 purge and trap after desorption. The GC was programmed at 35 °C for 5 min and 5 °C/min to 120 °C for 5 min. Standard curves were prepared from methanolic stocks spiked into distilled water. Quantifications were based upon linear least-squares equations relating sample peak area to standards.

3. Analysis of Pure Compounds by TOX. Solutions of pure halogenated organics, from methanolic stocks, were prepared in distilled water at concentrations of approximately 100 μg/L as chlorine; this is within the linear range of the TOX analyzer. Sodium sulfite was added (resulting in >0.3 mM solutions) to one of two 300-mL aliquots at 22–25 °C. The pH of samples was not measured or adjusted (according to standard methods) prior to the addition of Na_2SO_3. Only later, after it became apparent that pH had an effect on quantitation, was pH measured or adjusted. The pH of distilled water used in the laboratory was later observed to be in the range of ~6–7. Both solutions were analyzed for TOX after approximately 10 min.

4. Analysis of Pure Compounds by Gas Chromatography. Solutions of pure halogenated organics, from methanolic stocks, were prepared in distilled water at concentrations within the linear range of the ECD detector and were transferred to 100-mL serum bottles (Supelco 144). Sodium sulfite (1.6 mM) was added to one, ferrous sulfate (2.0 mM) to another, and no addition to the third bottle as a control. Bottles were capped with Teflon/rubber gas-tight septa to prevent loss of volatiles. Samples were stored at room temperature (18–20 °C) between replicate analyses.

5. Kinetic Studies. The kinetics of the reaction between 3-bromopropene and sulfite were examined at three pHs. The reaction of hexachlorobutadiene, at a single pH, was also monitored. Solutions of 3-bromopropene, from methanolic stocks, were prepared in phosphate-buffered distilled water at concentrations of 80–100 μg/L. Sodium sulfite was added (resulting in approximately 1 mM solutions). No sulfite was added to control samples. All samples were stored in headspace-free 4-dram vials at room temperatures (19.5 ± 0.5 °C for 3-bromopropene; 21 ± 0.1 °C for hexachlorobutadiene) until analysis by GC. Reactions were monitored up to 5 h. A control sample was analyzed at the end of each experiment.

Some decay was noted in control samples (0.0% bromopropene, pH 8.1; 9.3% bromopropene, pH 10; 12.5% bromopropene, pH 3; 1.8% hexachlorobutadiene, pH 8.8). Similar decay was noted in other control samples and may possibly be due to hydrolysis of the organic species.

6. Drinking and Reclaimed Water Samples. The water sources investigated during this study are summarized in Table I. To compare dechlorinating agents, aliquots (300 mL) of each sample were dechlorinated in excess with either sodium sulfite (~0.1 mM), sodium thiosulfate (~0.2 mM), or granular ferrous sulfate (~0.9 mM). Duplicates were analyzed for TOX after several minutes. To verify dechlorinating agent effectiveness, aliquots of a monochloramine blank, prepared by addition of hypochlorite to a bicarbonate-buffered (pH 8) ammonia solution, were dechlorinated with each chemical. TOX analyses indicated that no dechlorinating agent left a "carbon adsorbable" residual greater than 2.3 μg/L; this is within the error range associated with the method (*20*). An MWD sample was adjusted to pH 8.2 with sodium hydroxide, dosed with sodium sulfite (0.14 mM), capped, and allowed to react overnight (20 h). A control sample was dechlorinated, prior to analysis, with sodium thiosulfate (0.21 mM) as a control. Replicates of both samples were analyzed for TOX. Since pH appeared to be an important factor, additional samples from various sources were analyzed after dechlorination with sulfite at high and low pH. A sample aliquot was adjusted to pH < 2 with nitric acid and another to alkaline pH with several drops of ammonium hydroxide (if necessary). Both samples were dechlorinated with sodium sulfite (0.1 mM). After a reaction period up to several hours, the alkaline sample was adjusted to pH 2 with nitric acid and replicates of both samples were analyzed by TOX. To verify efficiency of dechlorination at pH extremes, a monochloramine blank (1.5 mg/L as Cl) was dechlorinated with sodium sulfite at both pH 8.7 and 1.5. No chlorine residual was detected in either sample by DPD analyses. TOX levels differed by 0.8 μg/L; this is within experimental error.

Table I. Water Sources

source	description
Santa Monica Treatment Plant	well No. 4 drinking water
Santa Monica Treatment Plant	well field composite drinking water
Metropolitan Water District	Central Project drinking water
Whittier Narrows Treatment Plant	reclaimed wastewater
UCLA Water Quality Lab	industrial tap water
Miramar Reservoir	untreated natural water
Castaic Lake	untreated natural water

7. Temporal Stability. The short-term temporal effects of sulfite addition to chlorinated water samples at various pHs were examined by using Whittier Narrows chlorinated effluent (total chlorine 0.48 mg/L, pH 6.9). Sodium sulfite (0.2 mM) was added to phosphate-buffered samples at pH 2, 6.9, and 10. A sample at pH 6.9 was used as a control and sulfite added only at the time of analysis. Samples were stored at 22 ± 1 °C and acidified aliquots analyzed at 0, 4, 24, and 72 h by TOX.

III. Results and Discussion

1. Pure Compounds. Nine of the 11 pure chlorinated compounds surveyed showed some degree of reactivity with aqueous sulfite (Table II). Groups were compared by an analysis of variance or one-tailed Students *t*-test. Statistically significant differences between sulfite-treated samples and control (no pretreatment and ferrous sulfate) were detected in 3-bromopropene (89% decrease; $\alpha = 0.005$), chlorobenzene (4.5% decrease; $\alpha = 0.01$), and bromobenzene (~3% decrease; $\alpha = 0.01$). It must be stressed that some of these reactions are time and pH dependent (see section on kinetics) and the data here are presented only to demonstrate reactivity at room temperature and short durations commonly encountered during chemical analyses.

2. Kinetics. Fam and Stenstrom (*7*) observed the reaction between aqueous sulfite and 3-bromopropene at room temperatures. They proposed a reaction involving nucleophilic attack by the sulfite ion at the halogenated carbon to produce an unsaturated sulfonic acid and bromide ion:

$$C_3H_5Br + SO_3^{2-} \rightarrow C_3H_5SO_3^- + Br^- \quad (1)$$

The kinetics of this reaction were investigated in this study, at various pHs. The kinetics of the hexachloro-

Table II. Effect of Dechlorinating Agents on Pure Compounds[a]

compound	dechlorinating agent	N	av TOX[b]	method of analysis
hexachloro-butadiene	none	2	118.72 ± 0.82[c]	TOX
	sulfite	2	99.35 ± 3.61	
dichloroacetic acid	none	2	88.20 ± 0.85	TOX
	sulfite	2	87.55 ± 1.63	
o-chlorophenol	none	2	104.75 ± 0.49	TOX
	sulfite	2	106.63 ± 0.48	
2-chloro-naphthalene	none	2	130.35 ± 1.77	TOX
	sulfite	2	126.25 ± 10.39	
trichlorobenzene	none	2	127.15 ± 0.07	TOX
	sulfite	2	115.95 ± 4.60	
dichlorobenzene	none	2	100.60 ± 1.13	TOX
	sulfite	2	95.80 ± 0.28	
hexachloroethane	none	2	84.40 ± 8.06	TOX
	sulfite	2	77.45 ± 0.64	
3-bromopropene	none	7	63.67 ± 6.84	
	sulfite	8	6.52 ± 14.13	GC/P&T
	ferrous sulfate	7	60.41 ± 7.02	
chlorobenzene	none	7	335.51 ± 9.30	
	sulfite	8	320.37 ± 8.92	GC/P&T
	ferrous sulfate	7	336.39 ± 12.64	
bromobenzene	none	7	56.27 ± 2.46	
	sulfite	8	54.66 ± 1.62	GC/P&T
	ferrous sulfate	7	57.79 ± 1.29	
trichlorophenol	none	4	155.20 ± 1.80	
	sulfite	4	151.90 ± 1.00	TOX
	ferrous sulfate	4	152.60 ± 3.10	

[a] Reaction time ~10 min; pH not measured prior to addition of dechlorinating agent. [b] Units, μg/L as Cl. [c] One standard deviation.

Table III. Kinetic Constants

compound	k, min^{-1}	pH	temp, °C
bromopropene	0.117 20 ± 0.0008[a]	8.1	19.4
bromopropene	0.117 55 ± 0.0005	10.0	19.2
bromopropene	not significant	3.0	19.5
hexachlorobutadiene	0.038 31 ± 0.0340	8.8	21.0

[a] One standard deviation.

butadiene/sulfite reaction were investigated at one pH level. If the above equation is first order with respect to the chlorinated organic and in $[SO_3^{2-}]$, the rate of disappearance of organic can be described by the equation

$$d[C]/dt = -k[SO_3^{2-}][C] \quad (2)$$

where [C] is the concentration of the organic. In the presence of excess sulfite, $[SO_3^{2-}]$ is assumed to be constant, and the term $k[SO_3^{2-}]$ is defined as a pseudo-first-order rate constant k. The pseudo-first-order rate constant k can be determined by plotting ln [C] versus time and using a linear least-squares method to fit the data (Table III). The decay of the bromopropene control sample at pH 3 (12.5%) was similar to decay of the terminal experimental sample (13.3%). Therefore, decay of the chlorinated organic, at this pH, could not be attributed to reaction with sulfurous acid species.

At alkaline pHs the reaction between 3-bromopropene and sulfite is rapid with a half-life of 5.9 min. In contrast, at pH 3 decay was not significant (Figure 1).

The distribution of sulfurous acid species, as a function of pH, can be calculated from dissociation constants (pk_1 = 1.796, pk_2 = 7.0) (*21*). At pH 3 the sulfite ion is an insignificant portion of the total sulfur concentration (~ 0.01%), while at pH 8.1 and 10.0 it comprises approximately 92.6% and 99.9%, respectively. The reaction of sulfite with hexachlorobutadiene, at high pH, has a half-life of roughly 18 min (Figure 2). As an estimate of the validity of this rate constant, it was used to determine the time required to obtain the reduction of hexachlorobutadiene observed in the above experiment (see Table II). The estimated time, 4.6 min, agrees well with the experimental protocol. The large amount of scatter associated with the plot is likely due to the small concentrations used (2.2 μg/L), dictated by the extreme sensitivity of the ECD detector to polychlorinated compounds.

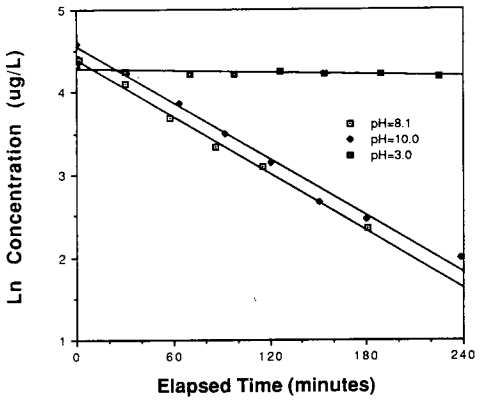

Figure 1. Bromopropene concentration versus time.

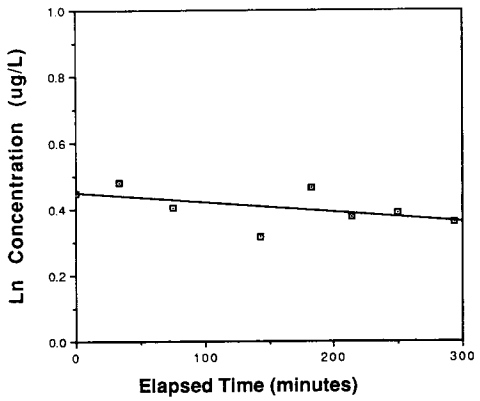

Figure 2. Hexachlorobutadiene concentration versus time.

3. Drinking and Reclaimed Water. Of the seven water sources surveyed for reactivity with sulfite, several showed significant reduction in TOX levels depending on dechlorination conditions. Sample groups were compared by a one-tailed t-test. The greatest difficulty in the design of this experiment was definition of an adequate control for TOX analysis. An ideal control would be chlorine residual free sample that contains the same level of TOX as the original chlorinated sample. Unfortunately, chlorine residuals must be removed prior to TOX analysis to prevent interferences due to the possibility of adsorption or reaction with activated carbon used in extraction.

After a survey of various dechlorinating agents, it became clear that ferrous sulfate and sodium thiosulfate were adequate dechlorinating agents and could be used for comparison. Sodium thiosulfate is not an ideal control because it is an extremely good carbon nucleophile (*21*). Ferrous sulfate is difficult to use since it is an excellent coagulant and occasionally clogs carbon columns during the extraction step. TOX levels were slightly lower in sulfite-treated samples than comparisons (using alternate dechlorinating agents) for Santa Monica Well and Metropolitan Water District samples. Little or no reduction was observed in UCLA tap water and reclaimed wastewater effluent from Whittier Narrows Treatment Plant. A statistically significant reduction in TOX (18.4%; α = 0.005) was observed between a sulfite-treated Santa Monica MWD sample (reaction time 20 h, pH 8.2) at room temperature and a control (sodium thiosulfate, reaction

Table IV. Effect of Dechlorinating Agents on TOX Analysis of Drinking Water and Reclaimed Water[a]

water	dechlorinating agent	N	av TOX[b]
chloramine blank	sodium sulfite	2	0.30 ± 0.71[c]
(1.1 mg/L total Cl)	sodium thiosulfate	2	2.35 ± 0.64
	ferrous sulfate	2	1.05 ± 0.07
UCLA tap	sodium sulfite	2	42.45 ± 0.92
(0.05 mg/L total Cl)	sodium thiosulfate	2	43.00 ± 0.85
	ferrous sulfate	2	42.40 ± 0.28
S.M. MWD	sodium sulfite	2	115.90 ± 0.28
(1.48 mg/L total Cl)	sodium thiosulfate	2	117.95 ± 1.06
	ferrous sulfate	2	136.70 ± 2.97
S.M. well composite	sodium sulfite	2	42.03 ± 0.52
(2.05 mg/L total Cl)	sodium thiosulfate	2	44.55 ± 3.46
	ferrous sulfate	2	51.69 ± 4.25
S.M. well No. 4	sodium sulfite	2	44.10 ± 1.98
(1.64 mg/L total Cl)	sodium thiosulfate	2	44.85 ± 3.46
	ferrous sulfate	2	52.60 ± 3.39
Whittier effluent	sodium sulfite	2	183.40 ± 5.80
(0.5 mg/L total Cl)	sodium thiosulfate	2	192.90 ± 8.77
	ferrous sulfate	2	178.65 ± 1.91
S.M. MWD	sodium sulfite[d]	7	88.00 ± 3.72
(0.92 mg/L total Cl)	sodium thiosulfate	7	107.90 ± 3.95

[a] Reaction time ~10 min; pH not measured prior to dechlorination. [b] Units, μg/L as Cl. [c] One standard deviation. [d] S.M. MWD sample dechlorinated with sulfite allowed to react at pH 8.2 for 20 h.

Table V. Effect of Sodium Sulfite on TOX Analysis at Various pHs and Reaction Times[a]

water	total Cl, mg/L	reactn conditns: pH	reactn conditns: time, min	N	av TOX[b]
S.M. MWD	1.5	1.5	135	2	131.50 ± 2.69[c]
S.M. MWD	1.5	8.2	135	2	98.10 ± 1.27
S.M. MWD+Br[d]	1.5	1.5	190	3	136.40 ± 4.45
S.M. MWD+Br[d]	1.5	8.7	190	3	96.67 ± 1.10
chloramine	1.5	1.5		1	14.80
chloramine	1.5	8.7		1	14.00
Miramar Res.	0.41	1.7	100	3	315.13 ± 12.37
Miramar Res.	0.41	9	100	3	197.67 ± 13.23
UCLA tap	1.66	1.5	60	2	112.70 ± 3.25
UCLA tap	1.66	8	60	2	96.84 ± 9.37
Castaic Res.	1.12	1.5	42	2	105.57 ± 15.50
Castaic Res.	1.12	7.6	42	2	94.60 ± 0.46

[a] Room temperatures (18–22 °C). [b] Units, μg/L as Cl. [c] One standard deviation. [d] KBr (78 mg/L) added and allowed to react overnight.

time <15 min, pH 7.9; see Table IV).

The most profound differences were observed between identical samples dechlorinated at low and high pH. TOX levels were lower in all water samples dechlorinated under basic conditions than replicates dechlorinated at pH < 2. Santa Monica MWD water TOX was reduced significantly (25.4%, $\alpha = 0.005$), as was the brominated sample (29.1%, $\alpha = 0.005$). The largest difference was observed in the Miramar Reservoir water (37.27%, $\alpha = 0.005$). Water samples that had been dechlorinated for less than 1 h differed less than 15%. Both initial TOX level and duration of reaction appear to be determining factors, suggesting a rate order of decay greater than zero (Table V).

The temporal dependence of the reaction of sulfite and the total organic halogen content of reclaimed wastewater, at various pHs, was explored. The reclaimed water samples, treated with sulfite, show a clear trend of decreasing TOX levels with increasing pH. This is in good agreement with other observations made in this study. Analysis of the control sample at pH 6.9, immediately after dechlorination with sodium sulfite indicated an initial TOX level of 171.9 μg/L. Analyses of experimental replicates at pHs 2, 6.9, and 10, after reacting for 15 min with sulfite, resulted in TOX levels of 193.2, 163.7, and 116.1 μg/L, respectively. Decrease of TOX of neutral and alkaline samples, over the 72-h period, (−9.46% pH 6.9, 22 °C; −13.4%, pH 10.0, 22 °C) did not differ substantially from the neutral control (−8.4%, pH 6.9, 22 °C). The acidic dechlorinated sample showed no decline over the period (+1.7%, pH 2.0, 22 °C). The results suggest that the reaction of halogenated organics with sulfurous acid species is more dependent upon pH than reaction duration.

IV. Conclusions

It has been demonstrated that significant reduction in TOX levels can result from dechlorination with sodium sulfite under pH neutral and basic conditions. The observed decay of organohalides in the absence of free chlorine may be caused by several factors: reaction with sulfites, reaction with other nucleophiles, spontaneous decay, or hydrolysis. However, the magnitude of decay of pure compounds at high pH in the presence of sulfite was much greater than controls and suggests that the sulfite ion is the reactive species toward certain organohalides. No method currently exists for dechlorinating samples without potentially altering integrity. It is suggested that samples requiring organohalide analysis be immediately analyzed after dechlorination at low pH.

Registry No. Hexachlorobutadiene, 87-68-3; dichloroacetic acid, 79-43-6; *o*-chlorophenol, 95-57-8; 2-chloronaphthalene, 91-58-7; trichlorobenzene, 12002-48-1; dichlorobenzene, 25321-22-6; hexachloroethane, 67-72-1; 3-bromopropene, 106-95-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; trichlorophenol, 25167-82-2; sodium sulfite, 7757-83-7; sodium thiosulfate, 7772-98-7; ferrous sulfate, 7720-78-7; water, 7732-18-5.

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