DECHLORINATION OF PCBS AND CAHS USING Na/NH_3: APPLICATION TO SOIL REMEDIATION

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ABSTRACT

PCBs and other chlorinated aromatic compounds are distributed in soils and sludges at over 400 sites in the USA. **CAHs** occur as serious contaminants at 358 major hazardous waste sites in the USA and they migrate vertically through soils to form DNAPLs on aquifer bottoms. Nitro compound wastes abound around amunition plants and nitration operations. Every state is represented in this problem. One example is DOEs Hanford site which has a groundwater carbon tetrachloride plume extending over 70 sq. miles. Many contaminated sites exist in the Gulf Coast region (Texas through Florida) where the largest concentration of chemical manufacturing plants in North America is located together with many DOD sites. Thus a national need exists for both *ex-situ* and *in-situ* methods to destroy these pollutants in soils and sludges rapidly at ambient temperature before they migrate into groundwater.

We have demonstrated that both Na/NH_3 and Ca/NH_3 solutions (solvated electrons) will dechlorinate **PCBs** and **CAHs** in seconds at ambient temperature even in the presence of excess water. PCB- and CAH-contaminated soils (as received clay, loam and sandy soils containing up to 25% water) were successfully decontaminated within 30 sec. at **25°C**. PCB and CAH destruction efficiencies **>99.9%** were achieved. Na/NH_3 was more efficient than Ca/NH_3. This advantage of Na vs. Ca increases as the H_2O/RCl increased. Rates of dechlorination of CCl_4, CH_3CCl_3 and some chloroaromatics were found to occur at diffusion controlled rates as demonstrated by reductions in Na-deficient environments. Intermediate dechlorinated products (such as $CHCl_3$ or CH_2Cl_2 were not observed in CCl_4 reductions. Only CH_4 and CCl_4 were detected. Chlorinated phenols (pentachlorophenol, 2,4,6-trichlorophenol and 2-chloro-4-fluorophenol) are all completely dechloronated at room temperature. We have now successfully **defluorinated** alphatic and aromatic fluorine compounds. Flourinated alkanes, upon treatment with $TiCl_4$, undergo immediate exothermic halide exchange producing insoluble TiF_3Cl and chlorinated hydrocarbons. These chlorinated species are then quantitatively dechlorinated in Na/NH_3 at diffusion controlled rates. This is the first practical method ever developed for rapid remediation of hazardous fluorinated aromatics. Note that $TiCl_4$ is a cheap commodity chemical which produces inert TiO_2 in the environment. Finally, nitroaromatic compounds have been successfully destroyed in model compound studies. Soil trials are planned in the near future.

The major goal is to develop solvated electron chemistry (e. g. Na/NH_3) as a single, multifunctional, portable technology applicable to both on site *in-situ* and on site *ex-situ* destruction of PCBs, CAHs, pesticides, herbicides, chemical warfare agents and munition/explosive residues. Even if only half of these classes of pollutants can be rapidly destroyed in solvated electron media, this single technology would have broad application.

INTRODUCTION

Halogenated organic compounds, such as solvents, pesticides, herbicides, PCBs, CFCs *etc.*, have caused serious environmental problems. PCBs, for example, are distributed in soils, sludges, estuaries, *etc.* at over 400 sites and chlorinated aliphatic hydrocarbons (CAHs) are serious contaminants at 358 major hazardous waste sites in the United States.

PCBs are regulated under TSCA (1). Chemical destruction has been carried out by incineration, wet air oxidation and catalytic dehydrochlorination reaction with superoxide, photolysis and electrolytic reduction. Metal-promoted borohydride or alkoxyborohydride reductive dechlorination (2), Ti-catalyzed borohydride dechlorination (3), iron-promoted dechlorination (4), borohydride reductive dechlorination in glymes (5) and thermolysis over solid bases like $CaO/Ca(OH)_2$ (6) were recently developed. However serious limitations exist and many methods cannot be used economically with soils.

Alkali metal-based reductive dehalogenation is a well known process. Knorre, etal added sodium to the halogenated organic compounds without solvent but this heterogeneous reaction is slow and moisture sensitive. Dissolving Li, Na, K or Ca in liquid NH_3 generates solvated electrons which dehalogenate dissolved organic compounds at exceptionally fast rates (8).

Both Commodore Solution Technologies (9, 10) and our group (11) have demonstrated that neat PCBs and PCB-contaminated soils (as received clay, loam and sandy soils containing up to 30% water) can be decontaminated in liquid ammonia slurries by adding Na or Ca. PCB-destruction efficiencies > 99.9% were achieved within 30 sec. at room temperature (9-11). These results indicate that Na/NH_3 or Ca/NH_3 dechlorinations are significantly faster than sodium's reaction with water. Soils typically contain water, oxygen and iron, all of which can interfere with solvated electron chemistry (12-14). Both oxygen and iron catalyze the reaction of Na and Ca with ammonia to produce the metal amide salt and hydrogen. The half-life ($t_{1/2}$) of solvated electrons in purified NH_3 is *ca.* 300 h (15), but in pure water the solvated electron has a $t_{1/2}$ of *ca.* 100 msec. (16). Dechlorination of PCB-contaminated wet soils is possible due to the relatively long solvated electron lifetime in 20% H_2O/80% NH_3 ($t_{1/2}$ = *ca.* 100sec. (15,17)) coupled with fast dechlorination by $Na/NH_{3(L)}$ (9-11). We recently published the first systematic study of solvated electron dechlorinations in $NH_{3(L)}$ with excess water present (18). PCBs, CAHs *etc.* intercalated deep in clay layers require diffusion of solvated electrons into soil or extraction of chlorinated organics into the bulk solution. This could allow time for competitive reactions with water. Competitive reactions may accelerate in the presence of oxygen, transition metal ions, acidic soil sites *etc.* Therefore, we determined the consumption of Na required to acheive complete dechlorination of both chloroaromatic and chloroaliphatic compounds in the presence of excess water, demonstrating that reasonable amounts of sodium would remediate both wet and dry soils (19). We now report that PCBs and dioxins can be remediated from contaminated sludges obtained from New Bedford Harbor using Na/NH_3. Furthermore, oils contaminated with PCBs and dioxins were successfully remediated. We also demonstrate that polynuclear aromatic hydrocarbons (PAHs) and fluorinated aliphatic and aromatic compounds can be destroyed by Na/NH_3. Furthermore, $TiCl_4$ reacts almost instantly with fluorinated aliphatic model compounds to give chloroaliphatics, which can be dechlorinated by Na/NH_3 at diffusion controlled rates.

RESULTS AND DISCUSSION

PCB- and Dioxin-Contaminated Sludges and Oils

The new Bedford Harbor Sawyer St. site in Massachusetts has been designated as a superfund site due to PCB contamination of river sediments. A sample of river sediment was first washed with diisopropylamine by the RCC B. E. S. T.^{TM} process to give an oil concentrate with a PCB level of 32,800ppm. Dioxins/furans (TEFs) were also present at 47,000ppt. The concentrate was treated with Na/NH_3 (Table 1). After treatment, the PCB level was only 1.3 ppm, well below regulatory requirements for disposal in non-hazardous waste landfills. Dioxins present were also readily remediated. This study also illustrates that the Na/NH_3 process can remove metals from substrates. The concentrate received was found to have lead, arsenic and selenium in high ppb levels. After treatment with the Na/NH_3 process, the PCB levels were below detection limits. The metals were removed from the solid matrix during transport of liquid ammonia from the reactor vessel. Metals were recovered from the ammonia recycle unit for fixing and disposal.

Decontamination of Oils

Contaminated transformer oils and cutting fluids have been readily remediated using Na/NH_3 (Table 2). Oils containing over 20,000 ppm of PCBs have been detoxified to levels below 0.5 ppm. Typically from 2 to 4% wt. Na in liquid NH_3 was used. The $NaNH_3$ was also used to remediate dioxins in waste oil from the McCormick and Baxter site in California. As shown in Table 3 dioxins were reduced to ppt (parts per trillion) levels.

Treatment of Polyaromatic Hydrocarbons with Na/NH_3

Pure samples of polyaromatic hydrocarbons (PAHs) are readily destroyed by solvated electrons in NH_3. Oligomeric Birch reduction type products are obtained. These reactions are slower than dehalogenation as was demonstrated by the rapid formation of benzene, toluene and napthalene in Na/NH_3 from their corresponding monochloro derivatives. Chlorine loss takes place before further reduction of PAHs occurs. Table 4 summarizes data on the destruction of pure PAHs where soils contaminated with PAHs were remediated to below detection levels. Mononuclear aromatics (benzene, toluene, anisole, nitrobenzene) undergo ring reduction according to the well known Birch reduction (12,17).

Decontamination of B4 Clay Soil Containing Lindane

A wet clay soil, type B4, was contaminated with 5000 ppm of the persistant pesticide lindane ($C_6H_6Cl_6$) and then treated Na/NH_3 at room temperature. Two grams of soil per 10 ml of NH_3 was the soil/ NH_3 ratio used. The stoichiometry of Na was varied between Na/Cl ratios of 4.16 to 12.5. Table 5 summarizes these results. When a Na/Cl ratio of 12.5 was used 87% of the Lindane was converted to benzene and 1,3-dichlorobenzene was the major isomer (11%) that remained. The use of larger amounts of Na allowed complete dechlorination to be achieved.

Defluorination of Aliphatic and Aromatic Fluorinated Compounds

The C-F bond is among the strongest bonds known. The bond dissociation energies (BDEs) of 1° C-F, 2° C-F and 3° C-F bonds are 447, 443 and 443 kJ/mole. These values are about 105 kJ/mole more than the corresponding BDEs of C-Cl bonds on the average. Thus, removing fluorine is difficult. Reductive defluorination of fluorinated compounds is a topic of current interest due to the increasing concern over accumulation of fluorinated compounds in the environment. Of particular concern are CFCs, fluorinated agriculture chemicals and industrial fluorinated compounds such as 3M Inc.'s Scotchgard^{TM} chemicals. For example, the estimated lifetime of perfluorocarbons in the atmosphere is more than 2000 years (20). The literature demonstrates that aryl and vinyl C-F bonds, while difficult to break, can be activated by transition and lanthanide metal complexes (21). Among the various defluorination procedures for polyfluoroaromatics, zinc reductions in aqueous DMF, (22) reductive defluorinations of pentafluorobenzonitrile by zinc in aqueous solutions (23) and reduction of pentafluorobenzoic acid in liquid NH_3 (24) are of particular interest due to the low cost of zinc. However, these methods only give partial defluorination. Not all C-F bonds are broken.

The defluorination of aliphatic and aromatic compounds by solvated electrons generated from alkali and alkaline earth metals in liquid ammonia now been accomplished in our lab. Na/NH_3 will defluorinate 1-fluorononane, 1-fluorooctane, fluorocyclohexane, fluorobenzene and fluorinated phenols. Furthermore, addition of $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $AlCl_3$, has been found to speed up the C-F bond cleavage in fluorinated phenols. It should be noted that fluorinated phenols provide an excellent test of reducing ability in basic media (e.g. NH_3) because acidic phenols are present as phenoxide anions in these media. Since they have a negative charge, phenoxide anions resist addition of electrons or nucleophiles.

Defluorination of Aliphatic Fluoro Compounds

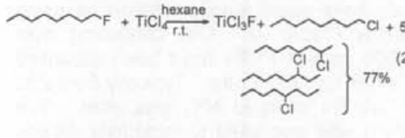
1-Fluorononane, a representative primary fluoroalkane, defluorinated slowly in Na/ NH_3 (equation 1). After 15 min. at room temperature only 39% fluorine cleavage occured in a 12 mole excess of Na. Only 13% cleavage occurred at 0 °C in 15 min. at this same excess of Na.

$$C_9H_{19}F + \underset{\text{(12 mole excess)}}{Na} \xrightarrow[\text{15 min.}]{NH_{3(l)}} C_9H_{20} + Na \quad (1)$$

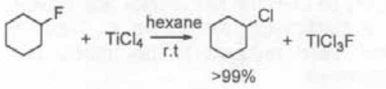
The activation energy was 11.4 kcal/mole based on the temperture dependence of the rate. While this defluorination can be carried to completion, the rate is far too slow to be useful in wet soils. Therefore, experiments were conducted to see if alkaline earth metals might not speed up defluorination. However, the rates using Ca/NH_3 and Sr/NH_3 were the same as those found in Na/NH_3 defluorinations (see Table 6). Thus, about 33-37% conversion to nonane occurred in 10 min. in all cases under the conditions used.

The defluorination of 1-fluorononane in Na/NH_3 was next studied in the presence of added metal salts including: $MgCl_2$, $CaCl_2$, $BaCl_2$, $AlCl_3$ and $TiCl_4$. The product distributions are summarized in Table 7. The only product produced was nonane when $MgCl_2$, $CaCl_2$, $BaCl_2$, or $AlCl_3$ were present. The rates were unchanged in the presence $MgCl_2$, $CaCl_2$, $BaCl_2$ (compare Table 6 and 7). The rate increased slightly in the presence of $AlCl_3$. However, a major change occurred upon adding $TiCl_4$ to 1-fluorononane. Cleavage of fluorine occurred rapidly when Na/NH_3 was added to $TiCl_4/C_9H_{19}F$. Some unknown products and 89% C_9H_{20} were obtained.

Further studies employing neat $TiCl_4$/1-fluorononane reactions revealed an explosively fast, exothermic reaction occurs between alkyl fluorides and $TiCl_4$. $TiCl_4$ exchanges chlorine into the alkane and rips out F to form $TiCl_3F$. The reaction proceeds with more fluoroalkane to eventually produce $TiClF_3$ and 3 RCl. This rapid F/Cl exchange proceeds through a cationic mechanism but it does not isomerize the hydrocarbon chain (see equation 2) in the reaction of either 1-fluorooctane or 1-fluorononane with $TiCl_4$. A similar reaction occurs with the model secondary alkyl fluoride, fluorocyclohexane (equation 3) and with α,α,α-trifluorotoluene (equation 4).



(2)



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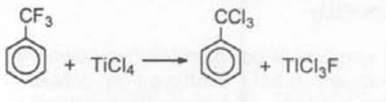
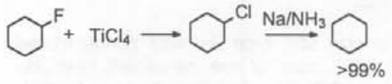


(4)

A very fast defluorination sequence to generate net F replacement by H can be obtained by a two step procedure. First, the fluoroalkane is reacted with $TiCl_4$ in an inert solvent (or neat) to generate the chloroalkane(s). Then the chloroalkane is dechlorinated by Na/NH_3 giving the alkane (net result is replacement of F by H). Equations (5) and (6) summarizes this two-step process for the model compound, 1-fluorooctane.

$$C_8H_{17}F + TiCl_4 \longrightarrow \underset{\text{mixture}}{C_8H_{17}Cl} \xrightarrow{Na/NH_3} \underset{83\%}{C_8H_{18}} + \underset{(17\%)}{\text{unknowns}} \quad (5)$$



(6)

$TiCl_4$ does not react with fluorobenzene or *p*-fluorotoluene. When $TiCl_4$ is mixed with *p*-fluorophenol only the *p*-fluorophenoxides of Ti were formed. These immediately regenerated *p*-fluorophenol on hydrolysis with water. Thus, the $TiCl_4$ reaction is selective to alkanes.

Defluorination of Aromatic Compounds

Fluorobenzenes were defluorinated by solvated electron reactions in liquid NH_3 where either alkali or alkaline metals are the electron source. Using three equivalents of Na, complete defluornation of fluorobenezene occurs as fast as the reaction can be run and quenched. Table 8 summarizes some results carried out with a stoichiometic deficiency of Li, Na, K, Ca, Sr and Ba. Calcium and sodium were the best metals for defluorination.

The cleavage of aromatic fluorines is not as fast as chlorine cleavage. This was illustrated during reductions of *p*-chlorofluorobenzene. When sufficient sodium was not available to remove all the halogens, more fluorine was found in the resulting products (Table 9). However this did not lead to a selective reduction procedure because the reactions are so fast they are close to diffusion control. Thus, when 2 equivalents of Na were used, benzene (35%) and *p*-chlorofluorobenzene (60%) were the major products. Chlorobenzene (0.2%) and fluorobenzene (3.4%) were also obtained.

Remediation of Soils Contaminated with Fluorobenzene or p-Chlorofluorobenzene

The B4 clay soil was contaminated with 5000 ppm of fluorobenzene or 5000 ppm of *p*-chlorofluorobenzene and then treated with Na/NH_3. As shown in Table 10, substantial reductions in these pollutants occurred. However, this work is preliminary and it is apparent that the levels of contaminate were still too high, requiring further treatment. In the case of B4 soil contaminated with *p*-chlorofluorobenzene, the removal of fluorine and chlorine was similar. This contrasts with the results of model compounds in solution. Perhaps some difference in soil binding exists when comparing these two models.

CONCLUSIONS

Solvated electrons react at diffusion controlled rates with CCl_4, CH_3CCl_3 and chlorinated aromatic compounds under the conditions applied. The addition of substantial amounts of water only modestly increased the amount of Na needed to completely dechlorinate organic substrates. Several types of PCB-containing wet soils and sludges can be decontaminated in >99.9% efficiencies with Na/NH_3 (this includes clays, sandy soils and organic soils). Sample soils from superfund sites were successfully decontaminated to levels below 1.0 or 2.0 ppm. Both PCB- and dioxin-contaminated sludge from New Bedford Harbor was remediated from 32,800 ppm (PCB) and 47 ppm (dioxin) to 1.3 and 0.012 ppm, respectively. Lindane, a persistant insecticide, can be remediated from soils using Na/NH_3. Dieldrin was remediated to levels <0.02 ppm in contaminated soils from two locations. Neat polynuclear aromatic hydrocarbons (PAHs) were destroyed in from 99.97 to 99.99% destruction efficiencies in single Na/NH_3 treatments. ***Thus, in addition to the demonstrated remediation of chloroorganic species from soils, we propose that this technology may be useful for remediating polynuclear aromatic hydrocarbons. Preliminary work reported last year (19) suggests nitro group-containing munitions wastes may also be successfully remediated.***

Solvated electron reductions can be used to defluorinate aromatic compounds and aliphatic compounds. The rate of fluorine cleavage from aliphatic compounds, however, is too low to effectively compete with the competiting reactions which destroy solvated electrons during soil treatment. But, to our surprise, a new reaction between $TiCl_4$ and fluorinated aliphatic molecules was discovered. Extremely rapid C-F cleavage occurs as F is exchanged for Cl. This led to a two step process to defluorinate RF to RCl followed by RCl dechlorination to RH. Exposure of RF to $TiCl_4$ produces chlorinated aliphatic compounds (RH) which are then dechlorinated to the corresponding hydrocarbons in Na/NH_3.

In all these dehalogenations the biproduct is the mineralized halide ion. Thus, chlorinated organic compounds give NaCl while fluorinated organic compounds produce NaF. The NH_3 is readily flashed from the soil and can be compressed and reliquified for reuse. The only ammonia residue in the soil/sludges is the NH_4^+ ion. Future studies will concentrate, at first, on PAH reductions. Will PAHs reduce effectively in the presence of water? This will be studied with model PAHs in defined NH_3/H_2O solutions where the amount of Na required to reduce all the PAH will be defined. Soils contaminated with PAHs will then be studied.

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Table 1. Na/NH_3 Treatment of PCB- and Dioxin-Contaminated Sludge from New Bedford Harbor

Contaminant	Pre-Treatment (ppm)	Post-Treatment (ppm)
PCB	32,800	1.3
Dioxin/Furan	47	0.012
Mercury	0.93	0.02
Lead	73	0.2
Selenium	2.5	0.2
Arsenic	2.8	0.1

Table 2. Destruction of PCBs in Oils by Na/NH_3

Material (Temp. °C)	Pre-Treatment (ppm)	Post-Treatment (ppm)
Motol oil (16)	23,339	<1.0
Transformer oil (40)	509,000	20[a]
Mineral Oil (40)	5,000	<0.5
Hexane (40)	100,000	0.5

[a] Sodium feed was deficient. Improved by adding more sodium. SET™ process.

Table 3. Na/NH_3 Treatment of Dioxins in Waste Oil at the McCormick and Baxter Site, Stockton, CA.

Contaminant	Before (ppt)	After (ppt)
Dioxins	418,500	2.3
Furans	14,120	1.3

ppt = parts per trillion

Table 4. Destruction of Neat Polynuclear Aromatic Hydrocarbons (PAHs) in Na/NH_3.

PAH	Pretreatment (μg)	Post-treatment (μg)	Destruction Efficiency (%)
Acenaphthylene	2005	ND[a]	99.99
Anthracene	1987	0.37	99.98
Benzo[a]pyrene	2007	0.56	99.97
Chrysene	2019	0.20	99.99
Fluorene	2013	0.14	99.99
Pyrene	2012	0.39	99.98

[a]ND = nondetected to limits of the analytical method.

Table 5. Remediation of Lindane from B4 Clay Soil Using Na/NH_3 at Ambient Temperature. Initial Lindane Concentration was 5000 ppm. The Na to Cl Ratio was 12.5[a].

Na/Cl	Products (% Conversion Based on Lindane						
ratio	Benzene	Chloro-benzene	1,3-Dichloro-benzene	1,2-Dichloro-benzene	1,3,5-Trichloro-benzene	1,2,5-Trichloro-benzene	1,2,3-Trichloro-benzene
4.15	37	-	5.1	0.4	2.6	48.4	6.3
6.67	72	0.4	9.0	0.3	0.8	15.3	1.9
9.17	80	0.2	10	-	0.5	9.0	0.5
11.67	86	-	13	-	-	0.4	0.1
12.50	87	-	11	2.2	0.1	-	-

Table 6. Product Distributions in 1-Fluorononane Defluorinations Using Different Solvated Electron Solutions Prepared from Different Metals (0.25 mmol of Fluorononane Was Used in Each Entry)[a]

Entry	Metal	Metal Usage	Product distribution (GC area%)	
		(mmol)	C_9H_{20}	$C_9H_{19}F$
1	Na	3	35.0%	65.0%
2	Ca	1.5	36.8%	63.2%
3	Sr	1.5	33.4%	66.6%

[a] The reaction were run for 10 min at room temperature with $NH_3(l)$ (10 mL) in each entry.

Table 7. Product Distributions for 1-Fluorononane Defluorinations by Na/$NH_3(l)$ at Room Temperature in the Presence of Different Salts.[a]

Entry	Salt	1-Fluorononane:Na:salt (mole ratio)	C_9H_{20} (%)[c]	$C_9H_{19}F$ (%)[c]	Unknown products (%)[c]
1	$MgCl_2$	1:12:4	38.1	61.9	ND[b]
2	$CaCl_2$	1:12:4	37.8	62.2	ND[b]
3	$BaCl_2$	1:12:4	37.7	62.3	ND[b]
4	$AlCl_3$	1:12:2	55	45	ND[b]
5	$TiCl_4$	1:12:2	89	1	10

[a] One fourth mmol of 1-fluorononane was used in each reaction in 10 mL of $NH_3(l)$.

[b] Not detectable.

[c] GC area percentage.

Table 8. Defluorinations of Fluorobenzene by Alkali or Alkaline Metals in $NH_{3(l)}$ at Room Temperature Using a Deficiency of Metal.[a]

Metal Used	$\frac{\text{Metal}}{C_6H_5F}$	Products (% Yield)			
		Benzene	Fluorobenzene	niline	1,4-Cyclohexa-diene
Li	2	77	23	-	-
Na	2	96	4	-	-
Na	2.5	99	1	-	-
K	2	58.5	39.3	2.2	-
Ca	1	98.2	0.3	-	1.5
Sr	1	67.3	30.2	-	2.5
Ba	1	59.4	26.6	-	13.9

[a] Complete defluorination occurs when the amount of metal was tripled.

Table 9. Defluorination of *p*-Chlorobenzene in Na/$NH_{3(l)}$

Temp. (°C)	Sustrate (mmol)	Na (mmol)	Products (% Yield)				
			Benzene	Chloro-benzene	Fluoro-benzene	Aniline	*p*-Chlorofluoro-benzene
23	1	4	97	-	-	2	1
23	1	2	35	0.2	3.4	-	60
-47	1	2	18	-	0.5	6.2	67
23	1	6	99	-	1	-	-

Table 10. Remediation of B4 Clay Soil Contaminated With Fluorobenzene or *p*-Chlorofluorobenzene Using Na/NH_3 at Ambient Temperature

Contaminant (conc.)	Na (mmole)	Na/X (mole ratio)	Products (% Yield)		
			Benzene	Fluorobenzene	Chloro benzene
Fluorobenzene (5000ppm)	20	20	98.4	1.6 (80ppm)	-
Fluorobenzene (5000ppm)	25	25	99.2	0.8 (40ppm)	-
p-Chlorofluoro-benzene (5000ppm)	30	15	90	6.3 315ppm)	3.6 (180ppm)
p-Chlorofluoro-benzene (5000ppm)	35	17.5	99.4	0.18 (9ppm)	0.34 (17ppm)