

# Studies on Degradation of Polychlorinated Biphenyls by Means of Fenton's Reagent

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## Abstract

Fenton's reagent was applied for degradation of selected congeners of PCBs (PCB28, PCB52, PCB101, PCB138) present in aqueous solution at ppb concentrations. The effectiveness of degradation by this chemical process was determined and the toxicity of degradation products was evaluated. The experiments lasted 96 hours under stable pH during the whole process. In 24 h intervals the samples were extracted and analyzed by GC, GC/MS and IC. At the same time the Microtox® test was applied to assess the toxicity of the resulting solution. It has been observed that the concentration of two congeners, namely PCB28 and PCB52, decreased rapidly within the first 24 h of the experiment, whereas the two remaining ones (PCB101, PCB138) were degraded poorly. After 96 hours of the process, apart from other oxygenated products, acetate and fumarate also were determined. Concentration of Cl<sup>-</sup> ions was only slightly increased, indicating that the substrates were not mineralized.

**Keywords:** PCBs, oxidation, toxicity, degradation

## Introduction

Polychlorinated biphenyls (PCBs) are synthetic, aromatic compounds that were quite massively produced during the past century [1, 2]. Due to their low biodegradability and extreme stability in the environment PCBs are classified into one of 12 groups of compounds named Persistent Organic Pollutants. During the period of their numerous applications these compounds have infiltrated the environment and have been reported as a considerable risk due to their toxic properties [1-4].

There are numerous studies on the environmental effects of PCBs showing that they have a tendency to accumulate in fatty tissue, which in turn makes them dan-

gerous for humans because they demonstrate mutagenous and teratogenous properties and increase the risk of cancer development [1, 3, 5-8].

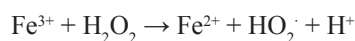
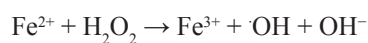
PCBs are now widespread in the environment at a very low concentration level. Thus, the fact that they are mostly present at ppb concentration levels causes significant analytical and toxicological problems [2, 9, 10].

Advanced Oxidation Processes (AOPs) are a group of emerging and promising techniques designed as a means of complete oxidation of numerous organic compounds such as chlorophenols [11, 12], phenols [13], pesticides [14-17], TCDD [18], dyes [19, 20, 21], and amines [22], as well as PCBs [23]. These processes rely on the generation of highly reactive oxygen species able to oxidize many organic compounds by non-specific radical processes. One of the AOP bases on hydrogen peroxide and Fe<sup>2+</sup> used to produce hydroxyl radicals is Fenton reaction. This reac-

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tion uses the oxidative power of the mixture composed of  $\text{Fe}^{2+}$  and hydrogen peroxide, a process in which  $\text{Fe}^{2+}$  ions are regenerated. Therefore, it is a catalytic process:



Hydroxyl radicals formed in Fenton reaction are characterized by high standard reduction potential in acid media, which in turn results in many cases in organic compounds being mineralized to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions [11, 24]. This characteristic prompted the use of Fenton reaction, as well as other oxidation processes, in industrial wastewater treatment processes [25].

Fenton reaction has already been applied for degradation of PCB congeners by several authors [23, 26-29]. It was used for degradation of mono-, di-, tri-, and tetrachlorobiphenyls present in commercial mixture of Delor 103 [23], and Aroclor 1242-contaminated sandy soil [26]. A variant of this reaction, namely the photo-Fenton process, was applied for degradation of some mono- and dichlorobiphenyls in aqueous solution [27], while electrochemical peroxidation process (ECP) as an enhancement of the classic Fenton's reaction was applied to the degradation of Aroclor 1248 [28, 29]. In these works an effort was made to study the influence of variable parameters of the process on its effectiveness understood as the disappearance of PCBs from the solution. Only in one case probable intermediates and products of PCB degradation were considered, whereas there are no data available on the toxicity of the products formed upon the oxidation process.

The aim of this study was to assess toxicity of products of PCB degradation by Fenton reaction applying Microtox Acute Toxicity Test, as well as to evaluate the efficiency of Fenton's reaction for the degradation of selected PCB congeners present in aqueous solution at ppb concentrations.

## Materials and Methods

### Sample Preparation

The solution of  $\text{FeSO}_4$  at a concentration of 200 mM was prepared in distilled water and pH was adjusted to 2.8 using 95% sulphuric acid.

125  $\mu\text{l}$  of each congener of PCB (PCB28, PCB52, PCB101, PCB138 – Riedel-de Haën) was spiked separately into a 100 ml serum bottle. The bottle was filled with distilled water at pH 2.8. Subsequently, 15  $\mu\text{l}$  of  $\text{FeSO}_4$  solution and 1 ml of  $\text{H}_2\text{O}_2$  (30%) was added. The serum bottles were placed in a rotary shaker (160 rpm) and the reaction was carried out in the dark at 23°C for 96 hours. After each 24 hours samples were extracted and analyzed.

Additionally, in each sample of pH, conductivity and concentration of  $\text{O}_2$  were determined electrochemically.

### Extraction

2.5 ml of hexane-containing PCB209 at a concentration of 39.2 ng  $\text{ml}^{-1}$  used as an internal standard, was added to the test solution in a serum bottle. The bottle was ultrasonicated for 30 min. After ultrasonication the samples were stored for 24 hours, during which phase separation occurred. The organic phase was transferred into a 4 ml glass vial and the extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$ .

### Analysis of Degradation Mixture

The collected extracts were analyzed on ELWRO N504 gas chromatograph, equipped with an electron capture detector (GC/ECD), in splitless mode. Nitrogen was used as a carrier gas at 1.2  $\text{cm}^3 \text{min}^{-1}$  flow rate. The gas chromatograph was fitted with fused silica capillary column Restek Rtx-5, 60 m length  $\times$  0.53 mm ID, film thickness 1.0  $\mu\text{m}$ . The temperature was programmed from 80°C (1 min) to 320°C (20 min), at a rate of 8°C  $\text{min}^{-1}$ .

For the purpose of identification of the degradation products, the extracts were analyzed on a Hewlett Packard 5890II Gas Chromatograph Mass Spectrometer 5971A with electron impact ionization EI. GC/MS operational conditions were as follows: the carrier gas was helium, injector: 250°C, detector: 280°C, capillary column Elite 5MS Perkin Elmer 25 m length  $\times$  0.20 mm ID, film thickness: 0.33  $\mu\text{m}$ , temperature program: 50°C (1 min) to 320°C (6 min) at the rate of 25°C  $\text{min}^{-1}$ , mass range: 35-550  $\text{m} \cdot \text{z}^{-1}$ .

The determination of chloride and the investigation of the degradation products was performed by means of ion chromatography (IC) with a conductivity detector (made by Hitachi). The ion chromatograph was equipped with Polysphere IC AN-1 column (Merck). The mixture of phthalic acid (Merck), boric acid (Merck) and tris(hydroxymethyl)aminomethane (TRIS, Merck) was used as the mobile phase at 1.3  $\text{cm}^3 \text{min}^{-1}$  flow rate, at 30°C.

### Toxicity Test

The test was applied to assess the toxicity of solutions obtained after completion of the degradation process. This test uses the strain of bioluminescent *Vibrio fischeri* in lyophilized form. In the presence of metabolism disruptive agents the decrease of luminescence is observed. The test was performed with the use of Microtox M500 analyzer with MicrotoxOmni software and *Vibrio fischeri* NRRL B-11177 strain (4H6002 series, expiration date 08.2006). The bioluminescent bacteria was supplied by Strategic Diagnostic Inc. (Newark, USA). The intensity

of light emission resulting from bacterial luminescence is measured after 15 min of incubation at 15°C. The test was carried out according to manufacturer's recommendation [30]. Sodium chloride solution at a concentration of 2% was used as a control sample. In order to remove toxic forms of active oxygen, 20 µl of 1N NaOH and 1 ml of 12% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>\*5 H<sub>2</sub>O (a. r. grade) were added to the solutions prior to toxicity determinations followed by acidification with 1N HCl to pH 6.0. The toxicity test was carried out 60 min after the addition of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>\*5 H<sub>2</sub>O. The results were calculated with the use of MicrotoxOmni software.

### Analysis of Gaseous Phase

The composition of gaseous fraction collected over the solution was analyzed by means of gas chromatograph equipped with a flame ionization detector (GC-FID) to determine hydrocarbons.

The instrumental parameters were as follows: the carrier gas-helium at 1.2 cm<sup>3</sup> min<sup>-1</sup> flow rate, packed column Poropak Q+S 2.5 m length, a temperature program: 80°C (1 min) to 220°C (5 min) at the rate of 5°C min<sup>-1</sup>.

The gaseous phase was analyzed for N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> using ELWRO 504N gas chromatograph with a conductivity detector (GC-TCD). The analyses were carried out under isothermal conditions – 60°C. CarbosieveB column of 2.5 m length was used.

The gaseous fraction was also analyzed on a Perkin Elmer AutoSystem gas chromatograph with an electron capture detector (GC-ECD) under isothermal conditions at 40°C. The capillary column Restek RTx-5 at 60 m length, 0.53 mm ID, 1 µm of film thickness was used.

### Results and Discussion

Commercial preparations contain complex mixtures of polychlorinated biphenyls and therefore their degradation is also a chemically complex process. Most probably the most important factor affecting the speed of oxidation of certain molecules of PCB is the number of chlorine atoms in its structure. Therefore, we have decided to study the effectiveness of the Fenton process using single, commercially available congeners of PCBs of variable structures, which are shown in Fig. 1.

According to literature oxidation efficiency of the Fenton reaction depends mostly on pH of the solution and Fe<sup>2+</sup>: H<sub>2</sub>O<sub>2</sub> molar ratio applied. Dercova et al. [23] showed that the most effective oxidation of PCBs solution in this reaction was achieved with Fe<sup>2+</sup>: H<sub>2</sub>O<sub>2</sub> molar ratio being 1:10000. In this study Fe<sup>2+</sup>: H<sub>2</sub>O<sub>2</sub> molar ratio 1:1000 had been applied. Results presented in Table 1 clearly show a gradual decrease in the concentrations of single congeners versus time of the process. It can be seen clearly that decomposition of all the congeners appeared to be most effective during the first 24 hours of the process. The rate of

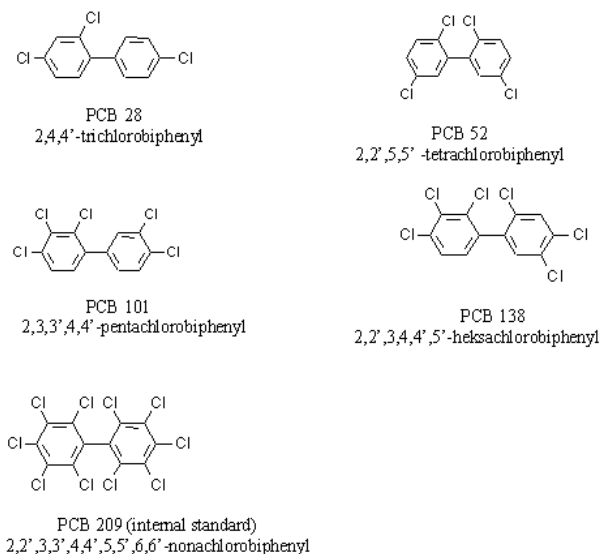


Fig. 1. Chemical structures of polychlorinated biphenyls and internal standard used in this study.

degradation is strongly dependent on chemical structure of the applied congener. Thus, in the case of low-chlorinated compounds their total disappearance was observed (level under the detection limit) after 96 hrs of the process. Pentachlorinated biphenyl PCB101 was degraded visibly faster than hexachlorinated PCB138. In the latter case 23% of the starting compound remained intact in the solution after 96 hrs of the process.

Since the starting concentration of the used PCBs is extremely low, the possibility that it is adsorbed on the surface of glass should also be taken into consideration. Such an effect was seen when studying oxidative degradation of 4-chlorobiphenyl [31]. Kuo and Lo [31] have also shown that degradation of 4-chlorobiphenyls is much faster than adsorption and that adsorption may be profitable in that it allows degradation to be achieved within a shorter period of time. Other studies showed that the degree of adsorption is related to the degree of chlorination and also depends on temperature and agitation [32]. Inten-

Table 1. Changes in PCB congener concentrations during 96 hour oxidation by Fenton reagent.

Time [ h ]	Concentration of congeners [ng ml <sup>-1</sup> ]			
	PCB28	PCB52	PCB101	PCB138
0	315.01	315.08	315.09	315.02
24	62.07	18.68	71.00	111.57
48	30.49	7.86	58.51	110.62
72	5.27	3.92	38.86	89.63
96	<0.98	<0.98	26.35	72.62

sive shaking of the reaction mixture applied in this study seems to prevent adsorption, at least as a major process.

Fig. 2 shows representative chromatograms obtained upon oxidation of PCB28 by Fenton reagent. In order to determine quantitatively the concentration changes an internal standard (PCB209) was added to the solution just before the analysis (peaks denoted 21 and 56 in Figs. 2A and 2B, respectively). As can be seen from Fig. 2A, hexane extract of the aqueous solution of the commercial agent PCB28 contains also quite significant amounts of unidentified impurities, which makes the analysis quite complex. Anyway, the detailed analysis of the chromatograms clearly shows that the starting PCB28 (peak denoted as 17 in Fig. 2A) quite effectively disappears from the solution, yielding a very complex mixture of products migrating faster in the applied conditions. This indicates that similar patterns of the process could also be observed in the case of PCB52, PCB101 and PCB138.

According to the results obtained with the oxidation of the PCB mixtures (Delor 103 and Alocor 1242) it is evident that chemical oxidation of the PCB congeners by Fenton reagent is non-specific and thus depends mainly on the number of chlorine substituents in the molecule rather than on their location [23], contrary to their biode-

gradation processes, which are structurally specific [33]. In our studies oxidation of individual congeners seems to be structurally dependent, which may be explained by the fact that there are no mutual influences between congeners. However, more detailed studies with the use of bigger number of congeners are required in order to generalize this finding.

In order to determine the status of solution at the beginning and at the end of the process the oxygen level, pH and conductivity were determined (Table 2). As can be seen from Table 2 all three parameters did not depend on the congener used and did not change the result of the process. An especially important finding is that conductivity remained at the starting level, which clearly indicates that chloride ions are not released from PCBs studied and therefore chlorine is still built up within the structures of resulting organic compounds. Ion chromatography supports this suggestion since the determined level of acetic and formic acids, as well as the level of chloride ions, was found to be only slightly over the detection limit.

During the process  $Fe^{3+}$  ions could form organic complexes with products of oxidative degradation. It is probable that these complexes are responsible for the interruption of the mineralization process [34, 35]. This, alongside

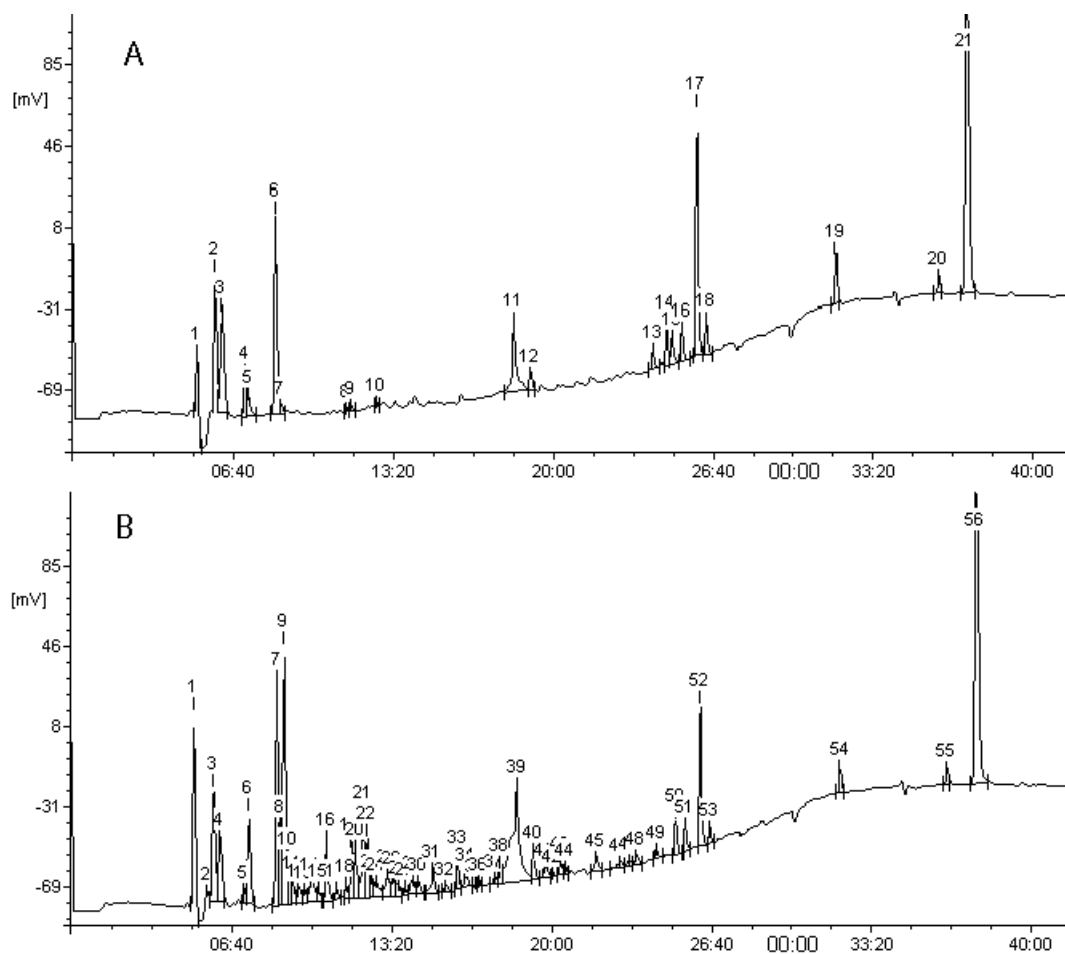


Fig. 2. Gas chromatograms of the extracts of: (A) congener PCB28 at the beginning and (B) after 24 hrs of the process. Peaks denoted 21 (chromatogram A) and 56 (chromatogram B) derive from internal standard PCB209.

Table 2. Changes of O<sub>2</sub> concentration, pH and conductivity measured before and after chemical oxidation.

Parameter	O <sub>2</sub>	pH	Conductivity
unit	[mg l <sup>-1</sup> ]		[mS cm <sup>-1</sup> ]
PCB28			
0 h	-	3.3	0.65
96 h	8.82	3.3	0.60
PCB52			
0 h	-	3.1	0.52
96 h	7.18	3.2	0.63
PCB101			
0 h	-	2.9	0.63
96 h	9.64	3.0	0.65
PCB138			
0 h	-	3.2	0.60
96 h	9.42	3.2	0.62

with extreme resistance of PCBs, disabled a complete oxidation of studied compounds.

We have additionally studied the composition of gaseous fraction collected over the solution. This fraction was found to contain carbon dioxide (which indicates that some part of the PCBs was mineralized) and, unfortunately, some low molecular chloroalkanes such as dichloromethane, trichloromethane, tetrachloromethane and trichloroethane. This finding indicates that precautions have to be undertaken since the gaseous products of PCB degradation might also be harmful for the environment.

Since the process was not complete the question about toxicity of the resulting decomposition products arose. In order to determine this we have applied standard Microtox® Acute Toxicity Test. This test is commonly used

Table 3. Toxicity data of Microtox test. TU toxicity unit.

Time	Sample TU=1/EC50*100				
	PCB28	PCB52	PCB101	PCB138	Fenton Reagent
0h	1.38	1.62	1.43	1.19	N
24h	1.19	1.27	1.45	1.65	N
48h	1.49	1.41	1.64	1.82	N
72h	2.02	1.85	2.18	2.11	N
96h	1.77	1.75	1.82	1.53	N

to assess the toxicity of industrial waste sediments [36], including sediments contaminated by PCBs [37]. The test was also used to assess toxicity of particular compounds [38], intermediates of photocatalytic decomposition of aqueous solution of 2,4-D [39], soils contaminated with pendimethalin and treated with Fenton reagent [40], wastewaters from pulp industry [41] and solutions of 2,4-D and 3,6-dichloro-2-methoxy-benzoic acid (dicamba) treated with ionizing radiation [42-44].

It is well established that hydrogen peroxide itself and reactive forms of oxygen might be toxic to bioluminescent bacteria. Therefore, the reactive oxygen species were removed by reacting with sodium thiosulfate prior to Microtox application. The blank sample of Fenton reagent after treatment with sodium thiosulfate did not show any toxicity towards a used microorganism (Table 3).

Results presented in Table 3 indicate that the toxicity of products of oxidation of all congeners is higher (in extreme cases doubled) than that of starting PCBs. Once more it supports the supposition that chlorine atoms remained in the structures of organic products obtained after their decomposition. It is worth noting that prolonged time of treatment increases toxicity of the resulting mixtures.

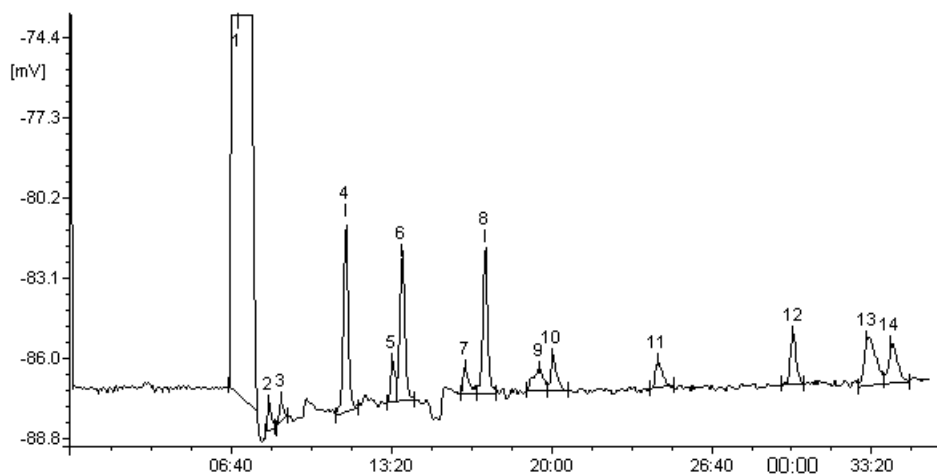


Fig.3. Chromatogram of gaseous fraction collected above PCB52 solution after 24h of oxidation. Amongst other unidentified compounds the following ones were determined: trichloromethane (peak 4), tetrachloromethane (peak 6) and trichloroethane (peak 8).

In order to identify PCB oxidation products GC/MS analyses of hexane extracts were also performed. Results of these analyses were ambiguous. Apart from the wide range of C6 and higher hydrocarbons we did not determine biphenyl, chlorophenols, chlorobenzenes and other chloroorganic compounds, which could be expected as degradation products. It suggests that the studied compounds were oxidized to a higher degree. It is also worth noting that commercially available PCBs were used as solutions in *isooctane* (10 µg ml<sup>-1</sup>), which also might be degraded by Fenton reagent and triggers the appearance of products of its degradation. Thus, the obtained set of products does not allow proposing any reasonable mechanism of that process.

### Conclusions

Fenton reagent is well established as both model system for studying the usefulness of oxidative process for xenobiotic degradation and as an industrial process for waste treatment. The results obtained in this study indicate that oxidation of PCBs might be a useful means for degradation of these toxic compounds. However, the Fenton process alone is moderately effective because, despite the fact that some derivatives were nearly completely decomposed (PCB28 and PCB52), they were not mineralized. Moreover, a chlorine atom remained in the organic parts of degraded compounds (most probably oxidized ones), which resulted in the increased toxicity of the complicated mixture obtained after the process.

As expected, the effectiveness of the process is strongly dependent on the structure of PCBs. Most obviously, the rate of degradation is strongly dependent on the number of chlorine atoms present in a molecule and probably on their location in the aromatic ring; however, more detailed studies with the use of bigger number of congeners are required in order to generalize this finding. PCBs are well recognized for their extreme resistance to chemical, photochemical and biological degradation. The studies presented in this paper have supported this observation. On the other hand, they have shown that oxidation might be a useful means for degradation of these compounds. However, a search for more vigorous and aggressive oxidizing agents and techniques is required.

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