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# OCCURRENCE OF LOW- AND HIGH-CHLORINATED PHENOLS IN MUNICIPAL SEWAGE BEFORE AND AFTER PASSING THROUGH BIOLOGICAL TREATMENT PLANTS

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## SUMMARY

Four biological treatment plants for municipal sewage, situated at different locations, were examined for their chlorophenol content and their ability to degrade these compounds. A routine method for the analysis of both low- and high-chlorinated phenols was developed, based on gas chromatography with electron-capture detection (GC–ECD). The method was evaluated by comparing the GC–ECD results with those obtained by combined gas chromatography–mass spectrometry with selected-ion monitoring of the molecular ions of the specific phenols. The total phenol content, determined by GC–ECD showed a good correlation with the phenol number, obtained by using the 4-aminoantipyrine method.

## INTRODUCTION

Chlorophenols are of great environmental concern as water pollutants in many countries[1–6]. Often they are both persistent and toxic[7,8] and have an unpleasant taste and odour, even in very low concentrations[9].

Chlorophenols originate from industrial synthesis or are unintentional by-products from industrial processes, such as the production of bleached pulp[10]. They are used, *e.g.*, as pesticides or as intermediates in the manufacture of chlorophenoxy acids, and the extensive use of chlorophenols has led to worldwide spreading of these compounds. Consequently, many analytical methods have been developed[7].

During a pilot study of the discharge of chlorophenols from a biological treatment plant for municipal sewage, which was known to receive industrial waste water containing chlorophenols, eight different chlorophenols were detected at low levels (in the following this plant will be termed plant I). In order to establish the significance of the chlorophenol discharge from the biological treatment plant, a study was conducted on four other Danish biological treatment plants, one in the centre of Copenhagen (plant II), one in the Greater Copenhagen area (plant III), one in a provincial town in Jutland with *ca.* 56,000 inhabitants (plant IV) and one in a provincial town on Sealand with *ca.* 29,000 inhabitants (plant V). None of these plants was known to be charged with industrial waste water containing chlorophenols. Also, the ability of the treatment plant to degrade chlorophenols was investigated. During the study, a routine method for the determination of both high- and low-chlorinated phenols by gas chromatography with electron-capture detection (GC–ECD) was de-

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veloped and tested against a gas chromatographic–mass spectrometric method based on selected-ion monitoring [GC–MS(SIM)].

## EXPERIMENTAL

### *Materials*

All solvents used were of Uvasol quality (E. Merck), sodium hydroxide was of Suprapur grade and other chemicals were of analytical-reagent grade. All chemicals were used as received, apart from sodium sulphate (dry), which was extracted with cyclohexane prior to use, and acetic anhydride, which was doubly distilled in glass.

### *Sampling*

During the pilot study, four effluent samples were taken as time-proportional samples from plant I. Then, two pairs of samples were taken from the influent and effluent of each of Plants II–V. These samples were taken as flow-proportional samples, one set during a weekend and another during the period from Monday to Friday.

All samples were preserved as prescribed by the Danish Standard[11].

### *Chemical analysis*

The total phenol content (the phenol number) was determined according to the Danish Standard[11]. Specific analysis of individual phenols was performed after extraction of acidified 500-ml samples with three batches of 100, 50 and 50 ml of *n*-hexane–diethyl ether (2:1). The volume of extract was reduced to 10 ml by evaporation in a Kuderna–Danish apparatus (recovery better than 90%, except for phenol and 2-methylphenol).

Non- and monochlorinated phenols were determined by GC–ECD after derivatization with pentafluorobenzoyl chloride by a slightly modified version of the method described by Renberg[12]. The phenols in a 2-ml aliquot of the 10-ml *n*-hexane–diethyl ether extract were extracted twice, each time with 2 ml of 1.0 *M* sodium hydroxide solution. The combined aqueous phase, containing the phenolates, was buffered with 8 ml of 1.0 *M* sodium hydrogen carbonate solution, pentafluorobenzoylated and extracted with *n*-hexane as described by Renberg[12]. No suitable internal standard was found. Normally, di- and polychlorinated phenols could not be acylated with pentafluorobenzoyl chloride. This is probably due to steric hindrance, and they were therefore determined as acetyl derivatives, also by GC–ECD. The phenols in a 4-ml aliquot of the *n*-hexane–diethyl ether extract were extracted twice, each time with 1 ml of 0.1 *M* potassium carbonate solution. The combined aqueous phase, containing the phenolates, was buffered, acetylated and extracted with *n*-hexane[5], adding 25 μl of a 2.5 mg/l aqueous solution of 2,4-dibromophenol as internal standard.

### *Apparatus*

GC–ECD was performed on the pentafluorobenzoylated phenolic extracts as well as on the acetylated phenolic extracts with a Hewlett-Packard Model 5840 gas chromatograph, equipped with a $^{63}$Ni electron-capture detector, an HP 7671A au-

tosampler and a capillary column splitless system. The capillary column was 25 m × 0.3 mm I.D. SE-54 fused silica (Hewlett-Packard). The carrier gas was hydrogen (2 ml/min) and the make-up gas was argon–methane (20 ml/min). The temperatures used were injection port 250°C, detector 250°C and oven 60°C for 0.6 min, then raised at 4°C/min to 300°C. The injection volume was 1 μl.

GC–MS(SIM) was performed on the acetylated extracts with a Hewlett-Packard Model HP 5995A GC–MS system.

The gas chromatograph was equipped with a Scientific Glass Engineering OCI-2 on-column injection system. The capillary column was 25 m × 0.3 mm I.D. DB-5 fused silica (J E W Scientific, California). The carrier gas was helium (1.5 ml/min) and the oven temperature was 70°C for 0.5 min, then raised at 10°C/min to 280°C.

The mass spectrometer temperatures were transfer line 250°C, ion source 150°C and analyser 180°C. SIM was run on underresolved peaks with a window size of 0.1 a.m.u. and a dwell time of 0.05 sec on each ion corresponding to the molecular ions of the acetylated individual phenols, monitored after loss of ketene $(M-42)^+$. This ion has the same structure as the original ionized phenol[13].

## RESULTS

Table I gives the results of the specific chlorophenol analyses from the pilot study, conducted on the effluent from Plant I. On this basis, it was decided to limit

TABLE I

CONCENTRATIONS (μg/l) OF THE CHLOROPHENOL COMPOUNDS FROM THE PILOT STUDY CONDUCTED ON THE EFFLUENT OF PLANT I

Sample dates and types and amounts of sewage per 24 h were as follows: A, 25.7.82 (holiday), 12,350 m³; B, 3.8.82 (production), 14,120 m³; C, 8.8.82 (production), 12,860 m³; D, 10.8.82 (production), 14,170 m³. The industrial holiday ended on July 29th.

| *Compound* | *A* | | *B* | | *C* | | *D* | |
|---|---|---|---|---|---|---|---|---|
| | *GC-ECD* | *GC-MS* | *GC-ECD* | *GC-MS* | *GC-ECD* | *GC-MS* | *GC-ECD* | *GC-MS* |
| 4-Chlorophenol | <d.l.* | <d.l. | <d.l. | <d.l. | <d.l. | 0.08 | <d.l. | 0.07 |
| 2-Chlorophenol | <d.l. | <d.l. | <d.l. | 0.06 | <d.l. | 0.30 | <d.l. | 0.25 |
| 6-Chloro-2-methylphenol | <d.l. | <d.l. | <d.l. | <d.l. | <d.l. | 0.20 | <d.l. | 0.12 |
| 4-Chloro-2-methylphenol | 0.5 | 0.28 | 5.2 | 5.1 | 5.9 | 4.8 | 2.9 | 2.3 |
| 2,6-Dichlorophenol | <d.l. | <d.l. | 0.11 | 0.11 | ** | 3.2 | 0.98 | 0.45 |
| 2,4-Dichlorophenol | <d.l. | <d.l. | 0.35 | 0.26 | ** | 0.32 | 0.20 | 0.23 |
| 4,6-Dichloro-2-methylphenol | <d.l. | <d.l. | 0.62 | 0.43 | ** | 3.0 | 2.0 | 1.8 |
| 2,4,6-Trichlorophenol | 0.08 | 0.09 | 0.92 | 0.66 | ** | 19 | 5.3 | 6.3 |
| g phenol/24 h | 5 | 3 | 63 | 59 | | 205 | 87 | 88 |

* d.l. = detection limit.
** The analysis failed.

TABLE II

CONCENTRATIONS (μg/l) OF THE SPECIFIC PHENOLIC COMPOUNDS FOUND IN THE INFLUENT AND EFFLUENT OF PLANTS II–V ON TUESDAYS AND SUNDAYS

| *Compound* | *Parameter* | *Plant II* | | *Plant III* | | *Plant IV* | | *Plant V* | |
|---|---|---|---|---|---|---|---|---|---|
| | | *GC–ECD* | *GC–MS* | *GC–ECD* | *GC–MS* | *GC–ECD* | *GC–MS* | *GC–ECD* | *GC–MS* |
| | Sample date (Tuesdays) | 2.11.82 | | 2.11.82 | | 9.11.82 | | 14.12.82 | |
| | Influent amount | 261,000 $m^3$ | | 70,900 $m^3$ | | 25,348 $m^3$ | | 6957 $m^3$ | |
| Phenol | | 13 | 46 | 3.2 | 6.7 | 1.1 | 2.6 | 2.0 | 3.1 |
| 2-Methylphenol | | 13 | —* | 0.88 | —* | 0.41 | —* | 0.20 | <d.l.** |
| 2,4-Dichloro-phenol | | 0.16 | 0.11 | 0.24 | 0.20 | 0.29 | 0.14 | 0.12 | <d.l. |
| 2,4,6-Trichloro-phenol | | 0.08 | 0.07 | 0.14 | 0.12 | 0.13 | 0.07 | 0.13 | ~0.2 |
| Pentachloro-phenol | | 0.24 | 0.35 | 0.39 | 0.46 | 0.67 | 0.43 | 0.17 | <d.l. |
| Total phenols*** | | 108 | | 85 | | 22 | | 110 | |
| | Effluent amount | 261,000 $m^3$ | | 70,900 $m^3$ | | 25,348 $m^3$ | | 7600 $m^3$ | |
| Phenol | | <d.l. | 0.35 | <d.l. | 1.1 | <d.l. | 0.44 | <d.l. | 0.90 |
| 2.Methylphenol | | 11 | —* | 0.85 | —* | 0.11 | —* | 0.05 | 0.12 |
| 2,4-Dichloro-phenol | | 0.08 | <d.l. | 0.33 | 0.25 | 0.23 | 0.12 | 0.03 | <d.l. |
| 2,4,6-Trichloro-phenol | | 0.09 | 0.06 | 0.18 | 0.15 | 0.17 | 0.08 | 0.08 | <d.l. |
| Pentachloro-phenol | | 0.19 | 0.27 | 2.4 | 2.2 | 0.67 | 0.34 | 0.09 | <d.l. |
| Total phenols*** | | 8 | | 36 | | 7 | | 38 | |

| | Sample date (Sundays) | 7.11.82 | | 7.11.82 | | 7.11.82 | | 12.11.82 | |
|---|---|---|---|---|---|---|---|---|---|
| | Influent amount | 206,000 m³ | | 63,200 m³ | | 22,338 m³ | | 5834 m³ | |
| Phenol | | <d.l. | 0.17 | 1.4 | 1.7 | 0.61 | 2.3 | <d.l. | ~0.1 |
| 2-Methylphenol | | 0.23 | —* | 0.16 | —* | 0.29 | —* | <d.l. | <d.l. |
| 2,4-Dichloro-phenol | | <d.l. | <d.l. | 0.12 | 0.10 | 0.09 | <d.l. | 0.02 | <d.l. |
| 2,4,6-Trichloro-phenol | | 0.04 | <d.l. | 0.15 | 0.12 | 0.11 | <d.l. | 0.04 | <d.l. |
| Pentachloro-phenol | | 0.19 | 0.15 | 0.18 | 0.34 | 0.52 | <d.l. | 0.18 | <d.l. |
| Total phenols*** | | 160 | | 44 | | 15 | | 100 | |
| | Effluent amount | 206,000 m³ | | 63,200 m³ | | 22,338 m³ | | 5834 m³ | |
| Phenol | | 0.90 | 0.91 | 0.42 | 0.64 | 0.97 | 0.99 | <dl. | 0.43 |
| 2-Methylphenol | | 0.36 | —* | 0.52 | —* | 0.11 | —* | 0.04 | 0.07 |
| 2,4-Dichloro-phenol | | 0.09 | <d.l. | 0.30 | 0.15 | 0.21 | 0.15 | 0.03 | <d.l. |
| 2,4,6-Trichloro-phenol | | 0.11 | <d.l. | 0.23 | 0.16 | 0.06 | <d.l. | 0.05 | <d.l. |
| Pentachloro-phenol | | 0.15 | 0.26 | 0.75 | 0.38 | 0.24 | <d.l. | 0.18 | <d.l. |
| Total phenols*** | | 7 | | 21 | | 11 | | 5 | |

* The ion at $m/z$ 108 was not considered in this GC–MS(SIM) analysis.
** d.l. = detection limit.
*** Determined by the 4-aminoantipyrine method.

the external standard analysis to the following eleven phenols: phenol, 2-methylphenol, 2-chlorophenol, 4-chlorophenol, 4-chloro-2-methylphenol, 6-chloro-2-methylphenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 4,6-dichloro-2-methylphenol, 2,4,6-trichlorophenol and pentachlorophenol. During the study, large amounts of 4-chloro-3-methylphenol were identified but not quantified. Table II gives the concentrations of the five phenols found in the influents and effluents of plants II–V during the periods from Monday to Friday and during weekends.

## DISCUSSION

### *Evaluation of the analytical methods*

The results obtained from the GC–ECD and the GC–MS(SIM) methods were comparable in most instances. However, the quantification of phenol by the GC–MS(SIM) method generally gave larger values than the GC–ECD method. Also, there was a lack of consistency between the methods for the determination of pentachlorophenol in the influent and effluent of Plant IV during the weekend. The GC–ECD results (0.52 and 0.24 μg/l, respectively) could not be verified by the GC–MS(SIM) analysis, as should be expected. Therefore, these values will be left out of the discussion.

The detection limits of the two methods are in the same range, 0.02–0.1 μg/l. The detection limits for the individual phenols by the GC–MS(SIM) method decrease with an increasing number of ions to be detected and an increasing number of chloro substituents in the phenols.

The sensitivity of the GC–ECD method for the individual phenols increases with increasing number of chloro substituents. With less than two chloro substituents, it becomes necessary to use a phenol derivatization technique specially aimed at ECD sensitization, *e.g.*, pentafluorobenzoylation, if ECD is to be used.

A comparative evaluation of the two methods shows that the GC–MS(SIM) method is the better for the determination of low- and non-chlorinated phenols, because this method has a slightly greater sensitivity, and an internal standard can be used. However, the GC–ECD method has a greater sensitivity for the higher chlorinated phenols.

The advantage that the GC–MS(SIM) method is free from errors caused by interfering compounds must be weighed against the advantages of the GC–ECD method, which is less costly with regard to instruments and more easily adapted to routine analyses.

More than half of the determined phenol concentrations were in a range less than ten times the detection limits of either method. Although the methods cannot be evaluated statistically on the basis of the present results, this leads to the presumption that the uncertainties of the analytical results are less than 50% for the lower concentrations and less than 10% for the higher concentrations.

### *Evaluation of results*

Six of the eight chlorophenols found in plant I are not found elsewhere above the detection limits (pentachlorophenol was not determined in plant I), and it is reasonable, therefore, to conclude that they are of specific industrial manufacturing origin. Hence they are not likely to be generally spread in the Danish environment.

Pentachlorophenol is known as a widespread contaminant[14–16]. It has been found in Denmark (together with 2,3,4,6-tetrachlorophenol) in mussels (1–5 ng/g dry weight), sediments (10–20 ng/g dry weight) and sea water (2–3 ng/l) in the Isefjord[17].

Pentachlorophenol in the effluent of sewage treatment plants has been reported at concentrations of 0.7–1.0 μg/l[4], which is a slightly higher level than that found in the present study. Earlier studies on sewage in Denmark showed a level of 0.2 μg/l[17].

The fact that during the period from Monday to Friday, the pentachlorophenol concentration increased in plant III, where it ranged from 0.4 μg/l (influent) to 2.3 μg/l (effluent), might be a result of biosynthesis in the plant, *e.g.*, if hexachlorobenzene is present in the influent, although possible contamination of the sample cannot be totally excluded. 2,4-Dichlorophenol has been reported in sewage at a concentration of 0.6 μg/l (ref. 4), and so was 2,4,6-trichlorophenol in the same study, although not quantitatively. Among other chlorophenols, these two have also been found in spent bleach liquors of the paper and pulp industry[10,18], but industries of this type do not discharge their wastes to the treatment plants investigated. Besides, the concentrations of chlorophenols in the sewage are generally very low.

Fig. 1 shows the levels of phenols in the influents and effluents of plants II–V, calculated from (1) the phenol number, (2) the sum of specifically determined phenols and (3) the sum of specifically determined chlorophenols.

The specifically determined phenols amount to about 15% of the total phenols (maximum 25%) in the influent, whereas the main components are other phenols, probably coming largely from natural sources, such as the degradation products of lignins and humic acids. The specifically determined phenols generally constitute a larger fraction of the total phenol content in the effluent, which means less efficient removal of these compounds. This is particularly true for the chlorophenols (with the exception of 4-chloro-3-methylphenol) and is in accordance with other reports[4].

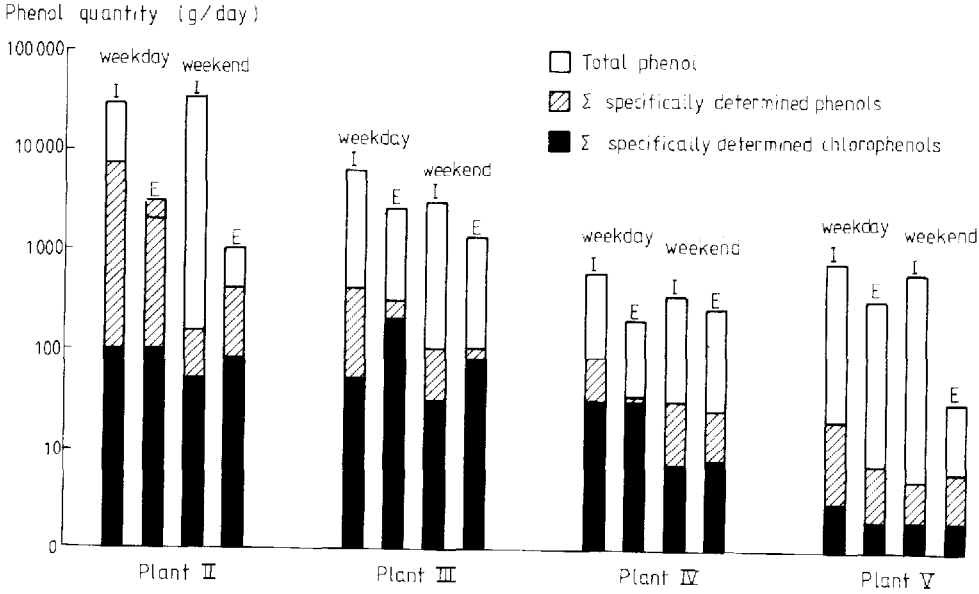


Fig. 1. Amounts of phenols in the influent (I) and effluent (E) of the four biological treatment plants.

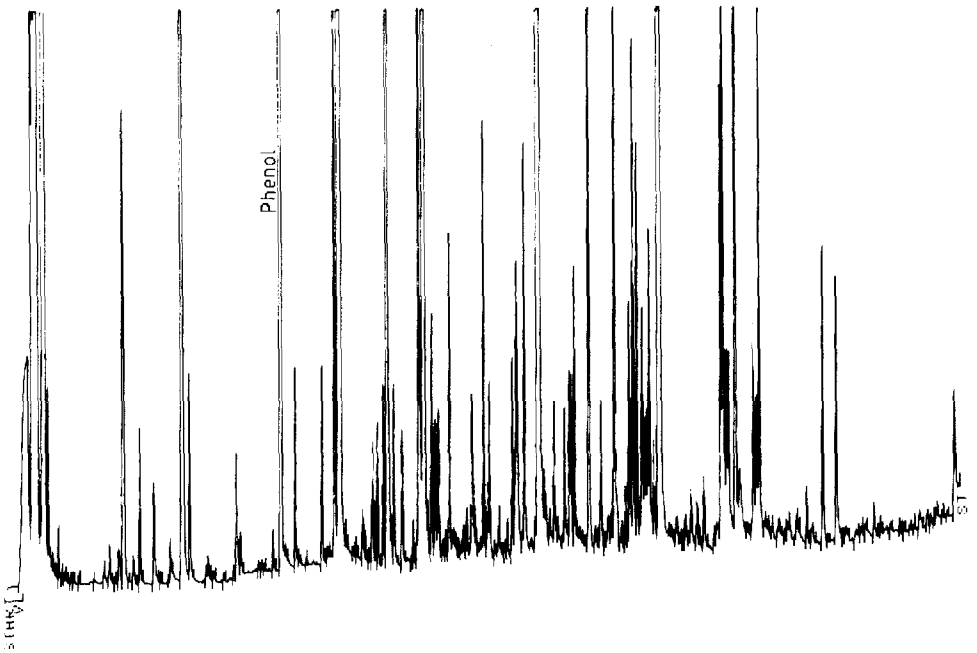


Fig. 2. Typical gas chromatogram (GC ECD) of the pentafluorobenzoylated extract of the influent to a biological treatment plant.

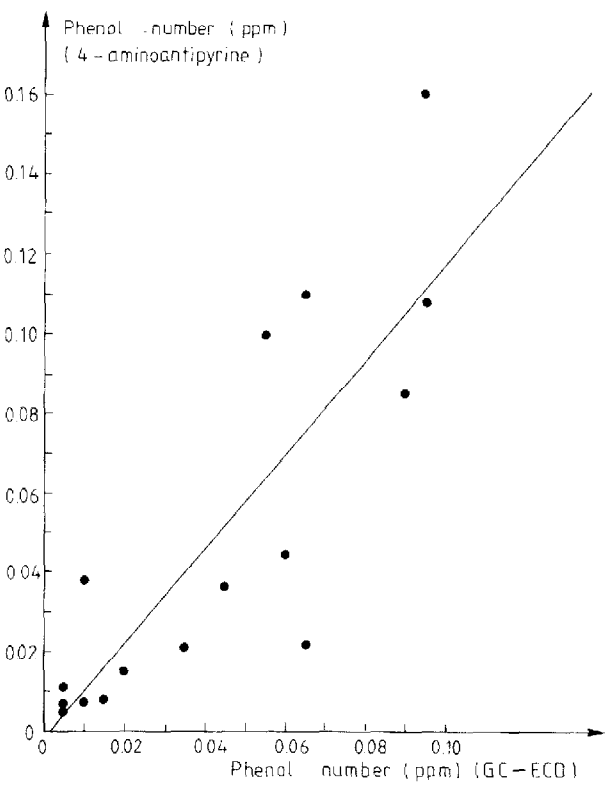


Fig. 3. Graph of the phenol number determined by the GC–ECD method against the phenol number determined by the 4-aminoantipyrine method. The regression line has a slope of 1.4 and a correlation coefficient of 0.84.

*Evaluation of the phenol number*

The chromatograms from GC–ECD of the pentafluorobenzoylated phenols show many other peaks (Fig. 2). Considering the isolation and derivatization techniques used, it would be reasonable to assume that these peaks correspond to specific phenolic compounds in the samples. The total peak area of the chromatogram, from the retention time of phenol onwards, converted into a phenol concentration by using the response factor for phenol, should therefore represent the total phenol concentration in the sample. Fig. 3 shows a plot of the phenol number, determined by GC–ECD and by the 4-aminoantipyrine method. There is a fair correlation between the two methods and a slope close to unity. Although the GC ECD method is too complicated for routine phenol number determinations, compared with the 4-aminoantipyrine method, it has the advantage of a lower detection limit, probably about 0.05 ppb ($10^9$) or less, and if one is to perform specific analyses for phenols by the pentafluorobenzoylation method the additional calculation of the phenol number by this method means little extra work. Analysis of drinking water for phenols by the 4-aminoantipyrine method is often very difficult owing to the very low maximum concentrations allowed (in Denmark the phenol number in drinking water must not exceed 0.5 ppb).

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