# Microporous PTFE Capillary On-Line Concentration Coupled To Flow Injection Analysis For Determination Of Propoxur

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## ABSTRACT

Capillary on-line linear concentration coupled with flow injection manifold was applied to determination of propoxur. The method is based on the alkaline hydrolysis of the pesticide and the resultant phenol is reacted with 4-aminoantipyrine in the presence of an oxidizing agent. The results showed that this method is simple and practicable, and is one of the most sensitive methods for the determination of propoxur. The linear range after concentration was between 0.2 $\mu g \cdot l^{-1}$ and 20 $\mu g \cdot l^{-1}$ for propoxur. The linear regression equation can be expressed by A=0.032c ($\mu g \cdot l^{-1}$) +0.0019(r=0.9996, n=9). The detection limit(three times the signal blank/slope) was 0.04 $\mu g \cdot l^{-1}$. The choice of concentration capillary and design for on-line concentration was studied carefully. The experimental conditions and reliability of the method was described exhaustively. The method is used to determine propoxur in spiked water samples. The recovery is between 92 % to 102 %.          © 2007 Trade Science Inc. - INDIA

## INTRODUCTION

Propoxur(isopropoxyhenyl methyl carbamate) is a carbamate insecticide that has wide applications in controlling numerous species of household and public health pests. In view of its wide application there is a need for the development of sensitive and reliable methods for the assessment of quality of insecticide formulations and to quantify the insecticide residues in water. There are spectrophotometric and other methods for the determination of propoxur. The spectrophotometric methods are most simple. They are based on the alkaline hydrolysis of the insecticide followed by coupling the resultant phenol with reagents such as 4-aminoantipyrine[1], 4-diaminodiphenyl sulphone[2], 3-methyl-2-benzoyhia

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zolinone hydrozone hydrochloride[3], p-dimethyl-phenylenediamine dihydrochloride[4], and 2-aminobenzophenone[5]. However, the sensitivity of these methods was less. The sensitivity of method can be increased by extracting the dye of hydrolysed phenolic product with 4-aminoantipyrine into small quantity of organic solvent[6]. But it is difficult for these methods to be applied to measure trace level propoxur.

Flow injection extraction in general has been shown to offer advantages with respect to low solvent consumption and improved precision of repetitive measurement. The sensitivity of existing methods is not yet high enough to reliably measure propoxur with concentration below a few parts per billion levels in real samples. In order to control such low levels, preconcentration of propoxur or phenolic product(the hydrolysate of propoxur) is necessary. There have reported the enrichment methods of phenol or its compounds, for example, liquid-liquid extraction[7], column chromatography[8], membrane filter[9], solid-phase extraction[10-11], capillary electrophoresis[12] and so on. The authors reviewed adsorbents for solid-phase extraction of phenol[13]. Non-polar reversed-phase adsorbents with silica base were the first materials tested in SPE of phenols in water, of which, $C_{18}$ is the most popular. $C_8$, cyclohexyl, phenyl and cyano are other silica-based adsorbents. Polymeric adsorbents have been developed by modification of earlier used XAD resins, and incorporated in commercial SPE device[14]. The authors prepared a porous structure fiber(Superox-4: polyethylene glycol) by the solgel method[15]. The linearity of the phenol is ideal in the range of $0.05\sim 1.0\mu g\cdot l^{-1}$. However, most of these methods lack the simplicity needed for routine analysis. Some of them either lack sensitivity and specificity or require extensive sample clean-up processes. It is necessary to improve these methods. For this purpose, the microporous PTFE(MPTFE) capillary is to be put forward as an adsorbent to concentrate the compound of hydrolysis product of propoxur with 4-aminoantipyrine. The results of our experiment show that it is simple and practicable.

## EXPERIMENTAL

### Apparatus and reagents

A flow injection system(Model FI-2100, Beijing Haiguang Instrument Co., China) was used for on-line analysis. An UV-Vis spectrophotometer(Unico 2000, Shanghai Unico Instrument Co., China) was used for absorbance measurement. One six-way injection valve fitted with a sample MPTFE capillary and an eluent tube. The common PTFE capillary of 1.0 mm(inner diameter) was used to construct the flow manifold except sample tube was made of MPTFE capillary(0.1×0.2×4.5 cm). MPTFE capillaries kindly provided by professor K.Watanabe, were used for the present study. Scanning electron microscopy of MPTFE capillary inner walls has been presented in figure 1

All reagents used in this study were of analytical reagent grade except the eluate. Eluate was of industrial alcohol. Water used was distilled one without containing phenol.

**Propoxur stock solution (1000$\mu$g·ml$^{-1}$):** Insecticide (0.10g) was dissolved in 100 ml of carbonyl free methanol. The stock solution was progressively diluted with the solvent to obtain standard solution of desired concentration (0.1g·ml$^{-1}$).

**Sodium hydroxide(2%):** Sodium hydroxide (2g) was dissolved in 100mL of distilled water.

**Color reagent:** 0.2 g 4-aminoantipyrine(4-AAP) was dissolved in 100 ml of distilled water respectively.

**Oxidant:** 0.8g of potassium ferricyanide was dissolved in 100mL of distilled water.

**Buffer solutions:** pH 5.1(HAc-NaAc), pH 6.0~pH 8.1 (KH$_2$PO4-Na$_2$HPO4), pH 8.6~pH 10.1(NH$_4$Cl-NH$_3$). The buffer solution of different pH were prepared and corrected by normal methods

### General procedure

Insecticide solution(10ml) was taken in a clean dry 100ml beaker. Two per cent sodium hydroxide solution(5ml) was added and allowed to stand for 5 min for complete hydrolysis; the pH of the solution is adjusted to 7.3 by adding 5ml buffer solution and the requisite amount of HCl and ammonia solution. Then 0.2% 4-AAP 0.5ml, 0.8% potassium ferricyanide 1.0ml were added into above flask respectively, and diluted to 100ml with distilled water. The mixed solution was laid aside for 10 min. Then the imine product was located in MPTFE capillary in front of

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the UV-Vis detector. Finally, the adsorbate was eluted to pass through the detector cell by a small volume of alcohol. The absorption value was recorded and calculated.

### Sample procedure

Lake water samples(100ml) spiked with 0, 0.2, 0.3, 0.4, 0.5 and 0.6μg of insecticide were taken, the pH of these samples adjusted to 3-4 with 2% sulfuric acid and 2g of anhydrous sodium sulphate. The mixture was transferred into a separating funnel and insecticide extracted using approximately 15ml of chloroform for each extraction by shaking 5-10 min. Combined extracts were washed with 2ml of 0.1M potassium carbonate to break any emulsion formed during the extraction, then dried over anhydrous sodium sulphate. Finally, chloroform was evaporated and residue dissolved in ethanol. Analysis was carried out using the above procedure.

### RESULTS AND DISCUSSION

### Choice of capillary and design for on-line concentration

The choice of capillary(as adsorbent) with high retention factors for phenolic species is of vital importance. MPTFE capillaries, a new special material, have good chemical and mechanical stability, fairly large pore size and large porosity, incorporate the advantage of membrane and column, and have higher velocity of mass transfer; more capacity of adsorption; less fouling and longer useful life[15]. Scanning electron microscopy of MPTFE capillary inner walls has been presented in figure 1.

Except the choice of capillary, the way of concentration or design is also of uppermost importance. To use the experience of other authors for reference, we considered the in-tube concentration with on-line flow injection analysis is a kind of efficient method. On-line can simplify the procedure and reduce errors of operation. In-tube, on one hand, is easy to achieve on-line design; on the other hand, is beneficial to concentration because the solution of samples is enriched into a small volume(about 0.04ml). But an efficient MPTFE capillary is a key to establish this method. The design of on-line in-tube concentra-
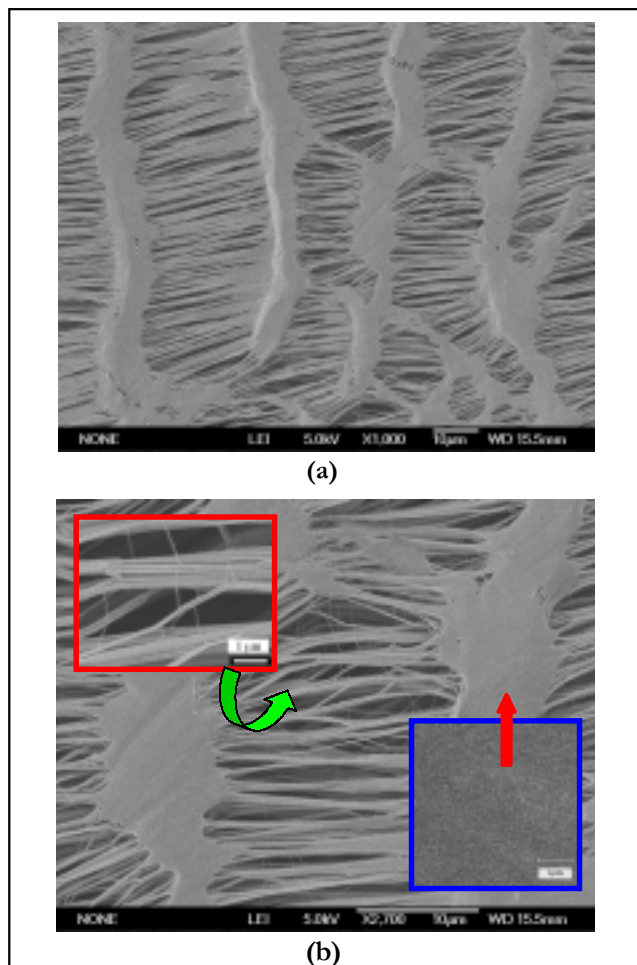


**Figure 1: (a) The SEM micrographs of unmodified MPTFE inner wall. (b) The partly magnified SEM micrographs of unmodified MPTFE inner wall**



**All straight line is teflon tube(inner diammter:1mm). Short straight line(on six-way valve)is sample.**
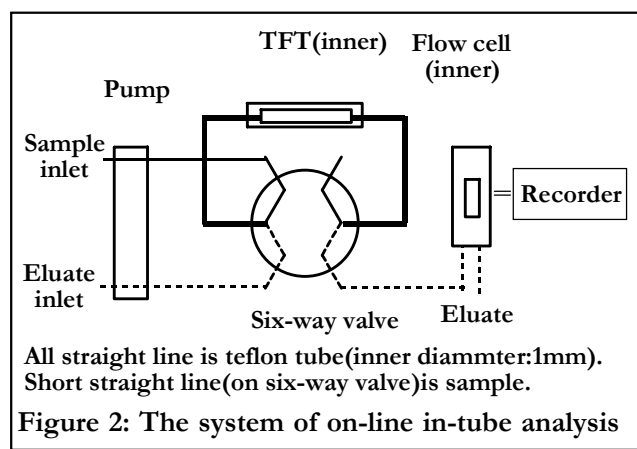
**Figure 2: The system of on-line in-tube analysis**

tion is as following:

In figure 2, thin straight lines stand for the state of sample concentration flow path; empty lines stand for the state of elution flow path; the thicker straight lines stand for the both state of sample concentration

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flow path and elution flow path. This kind of design is high efficiency because the volume of MPTFE capillary is very small(micro-liter), and is on-line in-tube.

Several kinds of tube materials were used to sorb o-isopropoxy phenol and the compounds of it with 4-AAP. The experimental results show that common teflon and nylon tubes don't sorb these above mentioned. PVC and silicon tubes have a weak absorption, but MPTFE capillary has strong absorption. The adsorbent equilibrium can get within 15min in the MPTFE capillary. So the MPTFE capillary is used as a adsorbent to carry out in-tube on-line analysis of propoxur.

## Color reaction of o-isopropoxy phenol with 4-AAP

The o-isopropoxy phenol(hydrolysis product of propoxur) can react with 4-aminoantipyrine(4-AAP), that was presented in figure 3. As a matter of fact, the detection of propoxur can be done by the determination of o-isopropoxy phenol. So we will discuss the effect factor on detection of phenols. The o-isopropoxy phenol is a polar compound. It was difficult to be adsorbed onto the surface of MPTFE capillary. However, the compound of phenols with 4-AAP over was easily adsorbed onto the MPTFE capillary because of its weak polar and the size of compound[16]. The mechanism of chromogenic reaction is as following:
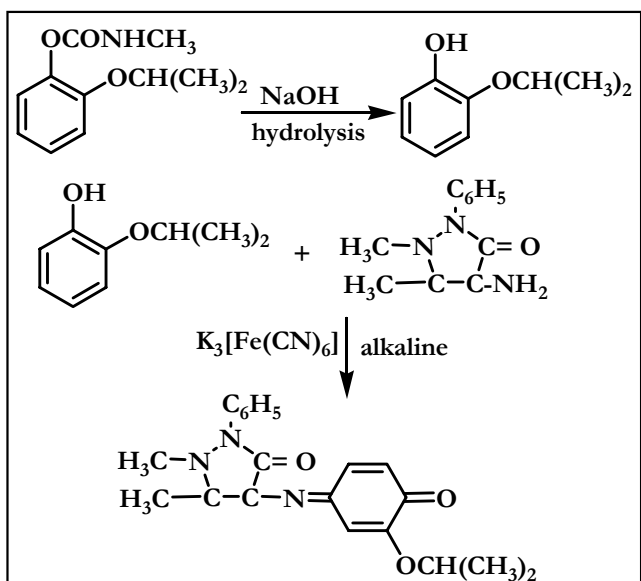


**Figure 3: The chromogenic mechanism of o-isopropoxy phenol with 4-AAP**

The maximum absorption of o-isopropoxy phenol with 4-aminoanitpyrine is 505 nm.

For getting best adsorbent efficiency, o-isopropoxy phenol reacts with 4-AAP in the presence of potassium ferricyanide to form an imine product. On one hand, the imine product has less polarity than o-isopropoxy phenol; on the other hand, the adsorbate will be diluted if the reaction occurs after concentration.

## Effect of pH and amounts of buffer solution

Figure 4 provided the effects of pH value and amount of buffer solution on this experiment. There is maximum absorption between pH 7.0~8.1. The pH range of optimum value is different with that of normal spectrophotometric determination. The possible reason is that it is beneficial to adsorption under the near neutral condition. The pH of 7.3 is chose as the usual procedure. There is maximum absorption between 0.25ml and 3.0ml. The 0.5ml is chose as the usual procedure.

## Effect of concentration of 4-AAP and potassium ferricyanide

There is maximum absorption between 0.25ml~0.95ml for 4-AAP and 0.50 ml~1.50ml for potassium ferricyanide. The efficiency of adsorption descended obviously when the volume of 0.2% 4-AAP is more than 0.95ml. There is adsorption contending between the compound of o-isopropoxy phenol and 4-AAP when the concentration of 4-AAP
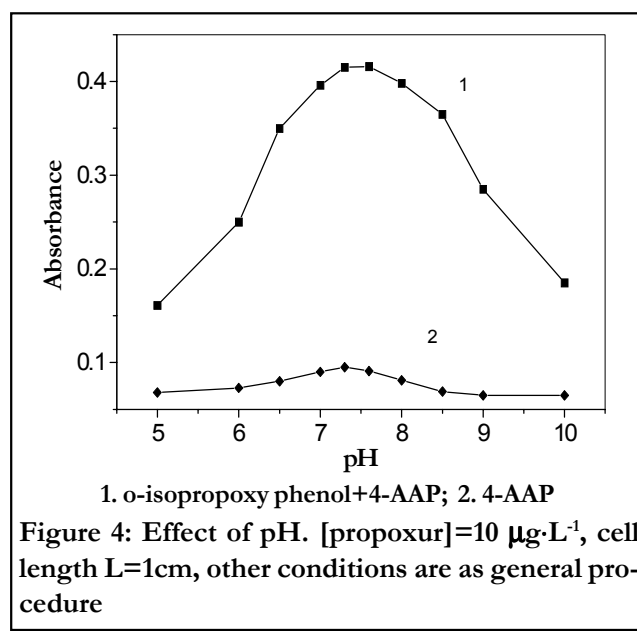


1. o-isopropoxy phenol+4-AAP; 2. 4-AAP
**Figure 4: Effect of pH. [propoxur]=10 $\mu g \cdot L^{-1}$, cell length L=1cm, other conditions are as general procedure**

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increases. The 0.50ml is chose as the usual proce-
dure. From above results, however, we found that
the concentration of potassium ferricyanide have less
effect on adsorption when its concentration is enough
to react with o-isopropoxy phenol and 4-AAP. The
reason is that potassium ferricyanide is not sorbed.
The 1.0ml is chose as the usual procedure.

### Effect of flow rate of sample and eluate

The efficiency of adsorption was enhanced while
the flow of sample increases. The greater the flow
rate increases, the more the amounts of sample passes
through the surface of MPTFE capillary at same time,
the less the time needed. But the flow rate between
$1.4ml\cdot min^{-1}$ and $1.8ml\cdot min^{-1}$ is advantage to stable
results. The flow rate of the eluate has a great effect
on the signal of monitoring. There are many irregular
peaks when the flow rate of eluate is rather small.
The stable results can be got when the flow rate of
eluate is greater than $1.6ml\cdot min^{-1}$.

### Effect of elution solvent and filter tube length

According to literature[15], the adsorbed phenols
could be recovered by eluting with an organic solvent
such as methanol, ethanol, acetone and ethylacetate
etc. However, in this study, we found most of these
solvents except for ethanol were unsuitable for the
system. There were irregular peaks when methanol
was used as eluate. The height of peak was obviously
descended when acetone was chose to elute the com-
pound. The acids can destroy the compound of o-
isopropoxy phenol with 4-AAP, so it can also not be
used as eluate. We chose alcohol as eluate in general
procedure.

We adopted several different tube lengths to as-
sess the effect of tube length. When a longer tube(8
cm) was compared with a shorter one(5 cm), the re-
ducing of the signal was believed to be a results of
dispersion. But too short a tube(<4 cm) resulted in
the irregular absorption peaks. That is because the
equilibrium of adsorption can not well achieved.

### Calibration curve, detection limit and repeata-
bility

Linearity was studied by pre-enriching through
filter tube. The linear range after enrichment about
25ml of sample solution was between 0.2~20 $\mu g\cdot l^{-1}$
for propoxur. The linear regression equation can be
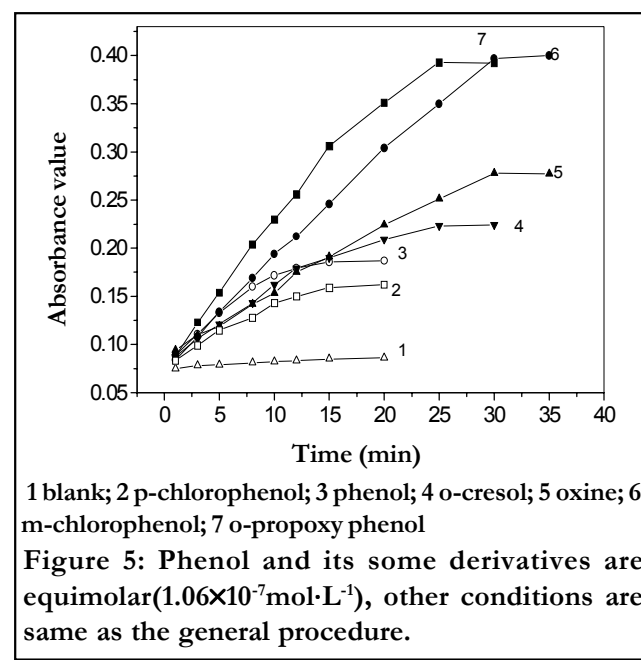
expressed by: A=0.032c+0.0019(r=0.9996, n=9),
where A is the measured signal in absorbance; c is the
concentration of the propoxur($\mu g\cdot l^{-1}$); n is the num-
ber of standard samples tested; r is the regression
coefficient.

Samples solution containing 0.5$\mu g\cdot l^{-1}$, 1.0$\mu g\cdot l^{-1}$
and 5.0$\mu g\cdot l^{-1}$ of proppoxur were used to study the
repeatability(n=7 or 8). The relative standard
deviations(RSD) of peak height were between 1.2%
and 2.2%. The results confirmed that excellent pre-
cision could be attained with on-line pre-concentra-
tion procedure described above. The detection limit
was estimated to be 0.04 $\mu g\cdot l^{-1}$.

### Response of phenolic derivations

The varying reactivity of substituted phenols
with 4-AAP is documented[7]. Little information,
however, could be found in the extractability of the
respective imine products formed[11]. The results of
our study are different with literature[7,11] due to the
difference of sorbent used to adsorb the compound
of phenols with 4-AAP.

It was presented in figure 4 that the response of
phenols. And enrichment factor of phenols and its
derivatives are shown in TABLE1. TABLE 1 the
factors of response and enrichment of o-cresol, o-
propoxy phenol, m-chlorophenol and oxine are ob-
vious higher than that of phenol. This may be more
hydrophobic compound to be compared with phe-



1 blank; 2 p-chlorophenol; 3 phenol; 4 o-cresol; 5 oxine; 6
m-chlorophenol; 7 o-propoxy phenol
**Figure 5: Phenol and its some derivatives are
equimolar($1.06\times10^{-7}mol\cdot L^{-1}$), other conditions are
same as the general procedure.**

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**TABLE 1: Enrichment factor of phenols and its derivatives**

| Phenols | Concentration $\mu g \, l^{-1}$ | Enrichment time (min) | Apparent molar absorption coefficient(mol$^{-1}$l cm$^{-1}$) | Enrichment factor* |
|---|---|---|---|---|
| Phenol | 10 | 15 | $1.2 \times 10^6$ | 100 |
| o-cresol | 11.5 | 25 | $1.5 \times 10^6$ | 150 |
| m-cresol | 11.5 | 25 | $6.0 \times 10^5$ | 90 |
| p-cresol | 11.5 | 15 | - | - |
| Oxine | 15.4 | 30 | $2.3 \times 10^6$ | 220 |
| Catechol | 11.7 | 20 | $2.9 \times 10^6$ | 50 |
| o-nitrophenol | 14.8 | 15 | $2.2 \times 10^5$ | 30 |
| p-nitrophenol | 14.8 | 15 | - | - |
| 2-aminophenol | 11.6 | 10 | $2.5 \times 10^5$ | 50 |
| Salicylic acid | 14.7 | 15 | - | - |
| m-chlorophenol | 15.6 | 25 | $3.5 \times 10^6$ | 220 |
| p-chlorophenol | 15.6 | 15 | $7.5 \times 10^5$ | 50 |
| o-propoxyphenol | 18.5 | 25 | $3.3 \times 10^5$ | 210 |

* Enrichment factor* is the ratio of absorption values after and before concentration

**TABLE 2: Studying of the determination interfere of propoxur by proposed method and normal FIA[10]**

| Interfering material | Normal FIA ($\mu g \cdot mL^{-1}$) | Proposed method ($\mu g \cdot mL^{-1}$) | Interfering material | Normal FIA ($\mu g \cdot mL^{-1}$) | Proposed method ($\mu g \cdot mL^{-1}$) |
|---|---|---|---|---|---|
| $Cl^-$ | - | >2000 | $Zn^{2+}$ | <1 | 10 |
| $CO_3^{2-}$ | 20 | >1200 | $Cu^{2+}$ | <1 | 5 |
| $NO_2^-$ | 5 | >600 | $Fe^{2+}$ | 10 | 2 |
| $NO_3^-$ | 20 | >800 | $Fe^{3+}$ | 10 | 1.5 |
| $SO_3^{2-}$ | <1 | 0.6 | Aniline | <5 | 0.2 |
| $PO_4^3$ | 20 | >600 | p-toluidine | - | 0.12 |
| $NH_4^+$ | 20 | >600 | o-phenyldiamine | <1 | 0.1 |
| $Mg^{2+}$ | 15 | >400 | p-sulfanilic acid | - | 0.20 |
| $Ca^{2+}$ | 15 | >400 | p-nitrophenyline | - | 0.05 |

[a] FIA*: the concentration of phenol is 0.5$\mu g \cdot mL^{-1}$; The proposed method:The concentration of propoxur is 5$\mu g \cdot L^{-1}$

nol. The m-cresol and o-nitrophenol etc have lower response due to the hinder of space frame.

## Study of interference

Some major inorganic species usually present in water were investigated as potential interfering materials with the phenol determination. The limits were taken as the largest amount of foreign species yielding a relative error(with respect to pure standard propoxur of 5$\mu g \cdot l^{-1}$) less than 5% in the peak height. TABLE 2 shows the tolerated limits for interfering materials accompanying propoxur of 5$\mu g \cdot l^{-1}$ using the proposed method and normal FIA. It allows us to conclude that almost all of ion and common species tested at their usual concentration in natural did not interfere with the determination.

The tolerated limits of aniline and its derivative are between 10 times and 40 times of propoxur. They will also react with 4-AAP under the presence of potassium ferricyanide when their concentration is enough for the reaction. Inorganic ions do not interfere the determination except for $SO_3^{2-}$ that is a reductive reagent. The interference of $Fe^{3+}$, $Fe^{2+}$ and $Zn^{2+}$ is due to their hydrolysis under the condition of proposed procedure when their concentration are several hundreds or thousands times the amounts of propoxur. $Cu^{2+}$ has interaction with 4-AAP or compound of phenols with 4-AAP under the presence of potassium ferricyanide. The mechanism of action remains to be solved further.

## Sample analysis

Water samples are prepared and determined as general procedure. Results are shown in TABLE 3. The

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**TABLE 3: Analysis of spiked water samples(n=5)**

| No. | Added(ppb) | Found(ppb) | Recovery(%) | RSD(%) |
|-----|------------|------------|-------------|--------|
| | | Spiked water | | |
| 1 | 0 | 0.25 | - | 2.9 |
| 2 | 2 | 2.02 | 100 | 2.1 |
| 3 | 3 | 2.85 | 96 | 1.5 |
| 4 | 4 | 3.69 | 92 | 2.0 |
| 5 | 5 | 5.12 | 102 | 2.2 |
| 6 | 6 | 5.95 | 95 | 2.6 |

results indicate that the recovery of propoxur from spiked water samples was quite satisfactory. The results further demonstrate that the method is suitable for the analysis of formulations and water samples.

### ACKNOWLEDGMENTS

### REFERENCES

[1] J.Piechocka, Rocz.Panstw, Zakl.Hig; **26**, 503-508 (in Polish); CA., **84**, 3369X **(1975)**.
[2] K.M.Appaiah, O.P.Kaurand, K.V.Nagaraja; J.Assoc. Offic.Anal.Chem., **66**, 105 **(1983)**.
[3] C.S.P.Sastry, D.Vijaya; Talanta, **34**, 372 **(1987)**.
[4] C.S.P.Sastry, D.Vijaya, D.S.Mangala; Analyst, **112**, 75 **(1987)**.
[5] D.Venkaiah, P.R.Naidu; Talanta, **37**, 629 **(1990)**.
[6] B.Venkateswarlu, K.Seshaiah; Talanta, **42**, 73 **(1995)**.
[7] A.Cladtra, M.Miro, J.M.Estelu; Anal.Chim.Acta, **421**, 155 **(2000)**.
[8] A.L.Moskin, L.N.Moskin, W.V.Moskishuchin; Talanta, **50**, 113 **(1999)**.
[9] S.Y.Sheikheldin, F.J.Cardwell; Anal.Chim.Acta, **419**, 9 **(2000)**.
[10] W.Frenzel, S.Krekler; Anal.Chim.Acta, **310**, 417 **(1995)**.
[11] M.V.Brijisvoort, S.K.Sanhi, H.Popke; Journal of Chromatography A, **757**, 165 **(1997)**.
[12] Y.S.Fung, Y.H.Long; Journal of Chromatography A, **907**, 301 **(2001)**.
[13] I.Rodriguez, M.P.Liompart, R.Lela; Journal of Chromatography A, **885**, 291 **(2000)**.
[14] E.G.Toledo, M.D.Prat, M.F.Alpenduradu; Journal of Chromatography A, **923**, 45 **(2001)**.
[15] G.Jin, A.Iburaim, M.Itagaki, K.Watanabe; Bunseki Kagaku(Japan), **52**, 171 **(2003)**.
[16] L.Zhang, G.Jin; J.Chromatog. B, **821**, 112 **(2005)**.