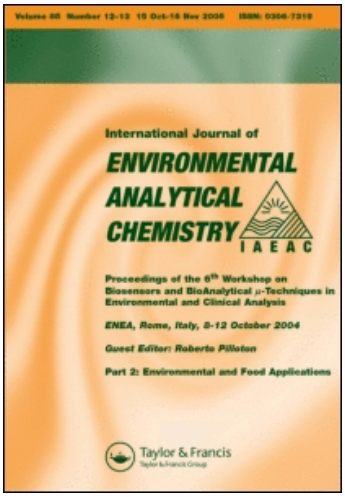

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Determination of Trace Amounts of Carbaryl in Water by Solid Phase Spectrofluorimetry

J. L. Vilchez[a]; R. Avidad[a]; A. Navalón[a]; J. Rohand[a]; L. F. Capitán-vallvey[a]
[a] Department of Analytical Chemistry, University of Granada, Granada, Spain

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DETERMINATION OF TRACE AMOUNTS OF CARBARYL IN WATER BY SOLID PHASE SPECTROFLUORIMETRY

J. L. VILCHEZ*, R. AVIDAD, A. NAVALÓN, J. ROHAND and L. F. CAPITÁN-VALLVEY

Department of Analytical Chemistry, University of Granada, E-18071, Granada, Spain.

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A simple and sensitive spectrofluorimetric method for the determination of carbaryl residues in water is presented. Carbaryl is hydrolized in alkaline medium to 1-naphthol. This hydrolysis product is fixed on QAE Sephadex A-25 gel at pH 11.20. The fluorescence of the gel, packed in a 1 mm silica cell, was measured directly using a solid-surface attachment. Spectral characteristics of 1-naphthol-gel system are described in detail. The applicable concentration range was 0.5–60.0 ng.ml^{-1}, with a relative standard deviation of 0.9% and a detection limit of 0.1 ng.ml^{-1}. The method was applied to the determination of carbaryl in natural waters.

KEYWORDS: Carbaryl, Solid-Phase Spectrofluorimetry (SPF), water analysis.

INTRODUCTION

Carbaryl (1-naphthyl-*N*-methylcarbamate) is one of the major pesticides used today as the active ingredient of widely used technical formulations[1-3]. Along with its relatively short half-life various studies have indicated that both carbaryl and its hydrolysis product 1-naphthol, may cause toxic effects by inhibition of cholinesterase enzyme and by their teratogenic character[4-6]. Therefore, the determination of carbaryl residues in natural waters is of great importance. Various methods have been proposed for its determination in formulations, crops, waters and soils. Usually, these methods involve a separatory technique such TLC[7-8], GC[9-10] or HPLC[11-17] in order to avoid matrix interferences. Several spectrofluorimetric methods have also been proposed for carbaryl determination based on its native fluorescence[18-21].

Fluorimetry offers an excellent detection limit in the determination of trace amounts of carbaryl, Solid-Phase Spectrofluorimetry (SPF) is a very valuable technique that shows some advantages such as: simplicity, low interference level, high selectivity, low detection level and the use of conventional instrumentation[22-28].

Dedicated to Professor Fermín Capitán García on his 72nd birthday.

* Author for correspondence.

In this paper a quick and sensitive method for the determination of carbaryl, *via* transformation in 1-naphthol, in natural waters using the SPF technique is proposed.

EXPERIMENTAL SECTION

Apparatus

The equipment consisted of a Perkin-Elmer LS-5 luminescence spectrophotometer, equipped with a Xenon discharge lamp (9.9 W) pulsed at line frequency, Monk-Gillieson F/3 monochromators, a Quantic Rhodamine 101 counter to correct the excitation spectra, a Houston Omnigraphic X-Y recorder, a Hamamatsu R298 photomultiplier and a Braun Melsungen Thermomix 1441 thermostat. In order to compare all the spectrofluorimetric measurements and ensure reproducible experimental conditions, the LS-5 spectrophotometer was checked daily. A *p*-terphenyl fluorescent polymer standard (10^{-7} M) gave a relative fluorescence intensity of 90% at λ_{em}= 340 nm, λ_{ex}= 295 nm (slit widths 2.5 and 2.5 nm; sensitivity factor 0.594). A Crison 501 digital pH-meter with saturated calomel and glass electrodes and an Agitaser 2000 rotating agitator were also employed.

To obtain three-dimensional spectra and contour plots in the excitation-emission plane, the LS-5 spectrometer was interfaced to a IBM PS/2 30-286 microcomputer using RS 232C connections. A BASIC program[29] allowed the acquisition of data and subsequent calculations. Pseudo-isometric three-dimensional plots were obtained using a hidden-line removal algorithm. The contour plots were produced by connecting points of equal fluorescence intensity by contour lines. The equifluorescence intensity points were calculated by linear interpolation between neighbouring points in the excitation-emission matrix, to find the (λ_{em}-λ_{ex}) pair corresponding to the contour fluorescence. An Epson LQ 550 printer was used for graphical representation.

Reagents

Carbaryl stock solution (100 mg.l^{-1}) Prepared by exact weighing of the reagent (Riedel-de Haën) and dissolution in ethanol. Working solutions were prepared by adequate dilution with doubly-distilled water.

1-Naphthol stock solution (100 mg.l^{-1}) Prepared by exact weighing of the reagent (Merck) and dissolution in ethanol. Working solutions were prepared by adequate dilution with doubly-distilled water.

QAE Sephadex A-25 dextran type anion-exchange gel (Sigma) was used in the chloride form and without pre-treatment in order to avoid contamination.

Fluorescence measurements

The measured relative fluorescence intensity (RFI) of the gel beads containing the fluorescent product packed in a 1 mm silica cell, was the diffuse transmitted fluorescence (DTF) emitted from the gel at the unexcited surface of the cell. The optimum angle formed between the cell plane and the excitation beam was 45° in all instances[30].

PROCEDURES

Basic procedure

A 500 ml sample water containing 0.5–60.0 $ng.ml^{-1}$ of carbaryl was transferred into a polyethylene bottle and 10 ml of 0.1 M NaOH solution and 100 mg of QAE Sephadex A-25 gel were added. The mixture was shaken mechanically for 10 min after which the gel beads were collected by filtration under suction and, with the aid of a pipette, were packed in a 1 mm silica cell together with a small volume of the filtrate. A blank solution containing all the reagents except carbaryl was prepared and treated in the same way as described above. The fluorescence intensities (20.0 ± 0.5 °C) of the sample and blank were always measured at λ_{em}= 450 nm with λ_{ex}= 333 nm (optimum spectral characteristics for 1-naphthol). A calibration graph was constructed in the same way using carbaryl solutions of known concentration.

Procedure for water

A volume of natural water sample containing an adequated amount of carbaryl was levelled off to 500 ml with doubly-distilled water, placed in a polyethylene bottle and 10 ml of 0.1 M NaOH solution and 100 mg of QAE Sephadex A-25 gel were added. The mixture was shaken mechanically for 10 min and then treated as described under Basic Procedure. The standard additions method was used for calibration purposes.

Treatment of the sample

Tap and natural water were filtered through a filter paper with a 0.45 μm size pore (Millipore) and collected in a polyethylene container that had been carefully cleaned with nitric acid. The samples were stored at 4°C until analysis. Analyses were performed with the least possible delay. The usual general precautions were taken to avoid contamination[31].

RESULTS AND DISCUSSION

Spectral characteristics

In Figure 1 the three-dimensional spectrum of the carbaryl hydrolized (1-naphthol) at pH 11.20 fixed on gel, after the blank substraction, is represented as an isometric projection, the emission spectra at stepped increments of the excitation wavelength having been recorded and plotted. Computer software allows the spectrum to be examined from a high- or low-excitation wavelength.

In Figure 2, the three-dimensional spectrum has been transformed into a contour plot in the excitation-emission plane, in order to ascertain both the excitation and emission maxima.

The peak wavelength in the emission spectra of carbaryl hydrolized-gel system is 450 nm and the excitation maximum is located at 333 nm. For optimum excitation and emission, slit-widths of 2.5 nm were selected in both instances.

From a study of the half-life of the excited state of the system in the solid phase at different temperatures, it was concluded that the luminescence process was fluorescence ($\tau<5\times10^{-6}$ s).

Hydrolysis and fixation process

A solution of carbaryl shows native fluorescence in neutral and acid media only, with maxima of excitation and emission at 279 nm and 333 nm respectively. Its hydrolysis product 1-naphthol exhibits fluorescence in basic media only showing excitation and emission maxima at 332 nm and 460 nm respectively.

Carbaryl is not fixed in presence of the QAE Sephadex A-25 at pH values <8.0. On the other hand, 1-naphthol is quantitatively fixed on QAE-gel at pH >11.0, showing fluorescence with maxima excitation and emission at 332 nm and 450 nm, respectively. When pH of carbaryl-gel is >11.0, the system show fluorescence with similar spectral characteristics to 1-naphthol-QAE gel.

The hydrolysis of carbaryl in presence of QAE-Sephadex start at pH 8.0 (Figure 3) and is complete at pH 11.0 in solution. However, the 1-naphthol in solution at pH >11.5 shows native fluorescence independent of pH values, whereas in gel phase a decrease of RFI takes place due to denaturation of gel.

The optimum pH for the simultaneous hydrolysis and fixation of the carbaryl was found to be within the range 11.0 to 11.5.

The effect of pH on carbaryl and 1-naphthol in solution and gel phase was studied using sodium hydroxide and hydrochloric acid for adjustment.

The hydrolysis order calculated in solution and gel phase is one. The presence of the gel produces an increase in the homogeneous rate constant (Figure 4).

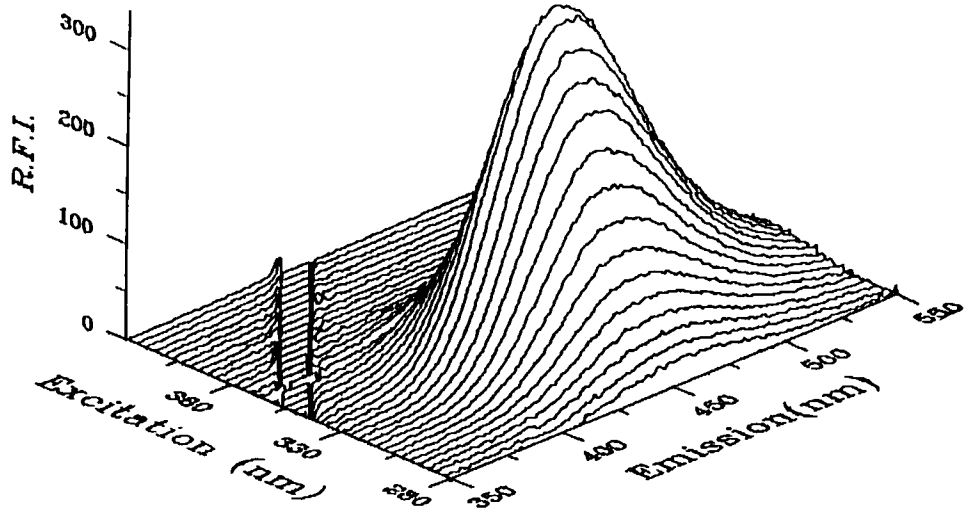

Figure 1 Projected three-dimensional spectrum of carbaryl.

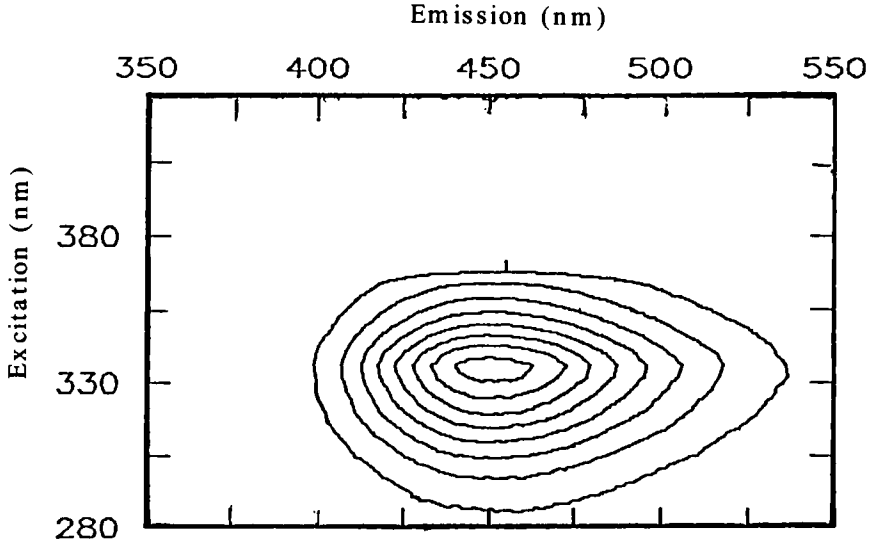

Figure 2 Contour plot of the excitation-emission matrix of the carbaryl at pH 11.20. The contour joints points showing the same relative fluorescence intensity.

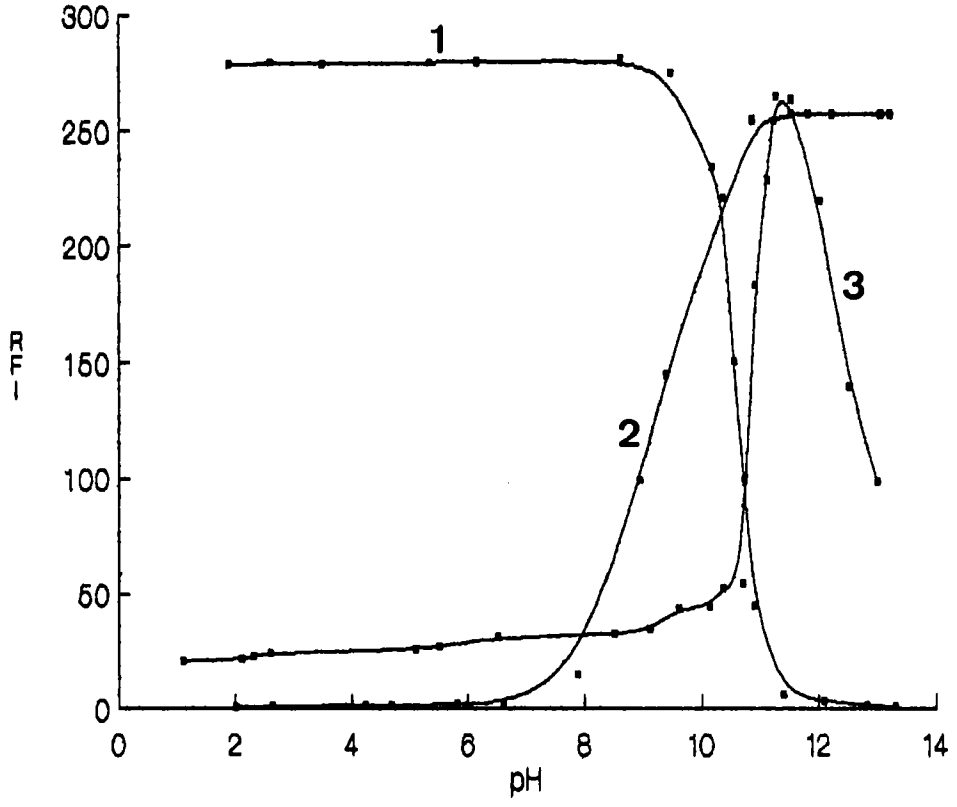

Figure 3 Influence of pH on relative fluorescence intensity of carbaryl: [1] 1.60 μg.ml^{-1} carbaryl aqueous solution, [2] 0.46 μg.ml^{-1} 1-naphthol aqueous solution and [3] 56.0 ng.ml^{-1} carbaryl-gel phase.

Optimisation of variables

The optimum pH for the simultaneous hydrolysis and fixation of the carbaryl was found to be 11.20.

Different buffer solutions, 0.05 M Na_2HPO_4-NaOH, 0.25 M KCl-NaOH and NaOH 0.1 M were tested. NaOH 0.1 M was found to be the most useful.

The fluorescence was independent of the ionic strength, adjusted with NaOH, NaCl and $NaClO_4$ up to 1.5 10^{-4} M.

The dependence of the RFI on the carbaryl concentration was linear; however, at higher carbaryl concentrations (60.0 ng.ml^{-1}) a quenching effect was observed probably owing to the re-absorbtion effect by solid matrix.

The shaking time necessary for maximum RFI development (performing the hydrolysis and fixation in the gel phase simultaneously) was 10 min for 100, 200, 500 and 1000 ml sample, being independent for higher times.

The effect of temperature on the fixation process and, hence, on the fluorescence emission was also studied. The measurements were carried out in the range 0–60 °C. The RFI

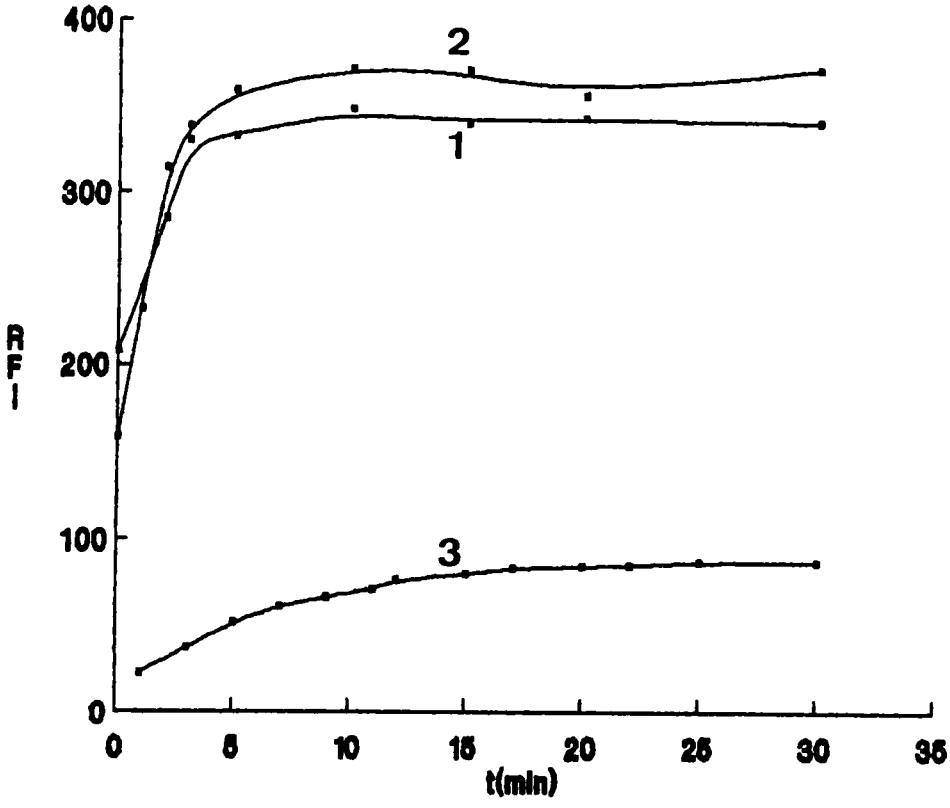

Figure 4 RFI vs shaking time on: [1] carbaryl-QAE, [2] 1-naphthol-QAE and [3] carbaryl solution phase. All measurements were performed at λ_{ex} = 332 nm and λ_{em} = 450 nm in gel phase and λ_{em} = 460 in solution phase.

decreased when the temperature of the system increased, the effect being totally reversible. The decrease in RFI was 0.2 % at 10°C, 0.8 % at 20°C, 9.1 % at 40°C and 15.2 % at 60°C. In this study the carbaryl fixation was carried out at 20.0 ± 0.5°C, the temperature selected for RFI measurements.

The addition order of the reagents did not affect the results obtained. The order used was carbaryl, buffer and gel.

As the use of a large amount of gel lowered the RFI, only the amount required to fill the cell and facilitate the handling (100 mg) was used in all measurements. With regard to the stability of the QAE-carbaryl system, the RFI remained constant for at least 1 h.

ANALYTICAL CHARACTERISTICS

Calibration and precision

The calibration graphs for samples treated according to the procedure described above are linear for the concentration range 2.0–150.0 ng.ml^{-1} for 100 ml, 1.0–90.0 ng.ml^{-1} for 200 ml, 0.5–60.0 ng.ml^{-1} for 500 ml and 0.1–50.0 ng.ml^{-1} for 1000 ml sample volume. The analytical parameters are summarized in Table 1.

The reproducibility of the proposed method and of packing of the gel in the 1-mm quartz cell was determined. The precision was measured for a carbaryl concentration of 30 ng.ml^{-1} by performing ten independent determinations.

The relative standard deviations (RSD) (p=0.05, n=10) were 1.3%, 1.2%, 0.9 % and 0.9% for 100, 200, 500 and 1000 ml sample volume, respectively.

The precision (RSD) of the packing operation, calculated for ten measurements, was 0.8% fixed in the gel, 0.8% for the gel blank (gel with buffer solution) and 0.8% for the gel alone. The precision (RSD) of the fluorescence measurements (noise) was about 0.5% in all cases.

Effect of sample volume on sensitivity

In previous papers it was mentioned that one of the advantages of SPF methods is the potential increase in sensitivity with an increase in the volume sample taken for analysis. This effect can be assessed by measuring the RFI of QAE gel equilibrated with different volumes of solution containing the same concentration of carbaryl and proportional amounts of the other reagents. The experimental data show a linear dependence of RFI *vs* sample volume in the range of 100–500 ml.

Sensitivity and detection limit

The sensitivity in this method can be enhanced by increasing the sample volume. This increase can be calculated from the slope of the calibration graphs. The calculated values

Table 1 Analytical parameters

Parameter	*Volume sample system (ml)*			
	100	*200*	*500*	*1000*
Intercept	0.8	0.2	-0.8	0.9
Slope	3.15	4.55	6.93	9.62
L. D. R. ([1]) ng.ml^{-1}	2.0-150.0	1.0-90.0	0.5-60.0	0.1-50.0
Correlation coefficient	0.998	0.999	0.998	0.999
Detection limit ng.ml^{-1}	0.3	0.2	0.1	0.1
Q. L. ([2]) ng.ml^{-1}	1.0	0.8	0.4	0.3
RDS (%)	1.3	1.2	0.9	0.9

[1]) Linear dynamic range.
[2]) Quantification limit.

of the sensitivity ratio for the samples analyzed were: $S_{1000/100} = 3.0$, $S_{1000/200} = 2.1$ and $S_{1000/500} = 1.4$, where the subscripts represent the sample volume (ml). The increase in sensitivity obtained with the proposed method respect to solution methods is significant.

The IUPAC detection limits (K=3), the quantification limits (K=10) and analytical sensitivities were calculated for 100, 200, 500 and 1000 ml sample volumes (Table 1).

Effect of foreign ions

A systematic study was undertaken of the effect of foreign ions and different pesticides, usually present in commercial formulations containing carbaryl, on the determination of carbaryl at the 15.0 $ng.ml^{-1}$ level. A 2 $mg.l^{-1}$ level of potentially interfering ions was tested first and, if an interference occurred, the ratio was reduced progressively until its disappearance. Higher ratios were not tested. Tolerance was defined as the amount of foreign ions inducing errors lower than ± 5% in the determination of the analyte. Table 2 shows the results obtained.

Applications

To check the accuracy of the proposed method, a recovery study was carried out on various types of sample waters. Tap water from the supply to Granada (Spain) and mineral water from Ortigosa del Monte (Spain), were analised after adequate additions of carbaryl. The volume of water used was 500 ml in all instances. Carbary aliquot additions from 2 to 30

Table 2 Effect of foreign ions on the determination of carbaryl.

Foreign ion	*Tolerance level* ($\mu g.ml^{-1}$)
ClO^-	30
Cl^-, ClO_4^-, Cd^{2+}	10
F^-, PO_4^{3-}	8
EDTA, Br^-, NH_4^{1+}	6
SO_4^{2-}, CO_3^{2-}	2
HCO_3^-	0.7
NO_3^-	0.6
Ca^{2+}, Mg^{2+}, Mn^{2+}	5
Al^{3+}	1.2
Cu^{2+}	0.3
Cr^{3+}	0.08
Fe^{3+}	0.014
Lindane[1]	2.25
Captan[1]	1.1
Thiabendazole[2]	0.212
Dichlone	0.04
o-Phenylphenol[2]	0.001

1: non fluorescent pesticide
2: fluorescent pesticide

Table 3 Study of carbaryl recovery in water samples.

Water	*Added (ng.ml^{-1})*	*Found (ng.ml^{-1})*	*% Recovery*
Tap	10.0	9.9	99.0
(Granada	20.0	20.1	100.5
City)	30.0	29.9	99.7
Mineral	10.0	10.0	100.0
(Ortigosa	20.0	20.1	100.5
del Monte)	30.0	30.1	100.3

ng.ml^{-1} of around 5 ng.ml^{-1} each were carried out. For the levels of the ions summarized in Table 2 no interferences with carbaryl recovery were detected. The usual chlorine level in tap water (0.6 ng.ml^{-1}) did not produce interferences either.

Moreover, the average percentages of recovery of the spiked waters, mean of three determinations, were acceptable within the standard conditions established as shown in Table 3.

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