

Determination of organophosphorous pesticides in deo-distillates from physical oil refining process

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Introduction

The decontamination of oils by refining is well known. Undesirable products like pesticides and PAHs are eliminated at different steps during the refinery. In particular, the deodorization step removes completely organo phosphorous pesticides from oil in case of chemical refining as in case of physical refining. Deodorization consists in submitting oil under vacuum at temperature between 180 and 270°C and high pressure vapour stream. The by-product of this process is free fatty acids distillate in which pesticides are suspected to be concentrated.

The purpose of this work was to develop and validate a method for the determination of organo phosphorous pesticides in deodistillates from refining.

Materials and Methods

Samples

- 1) Deo-distillate of physical refining of crude sunflower oil used to develop the method .
- 2) Sunflower free fatty acids, used to validate the method.

Extraction and clean-up procedure

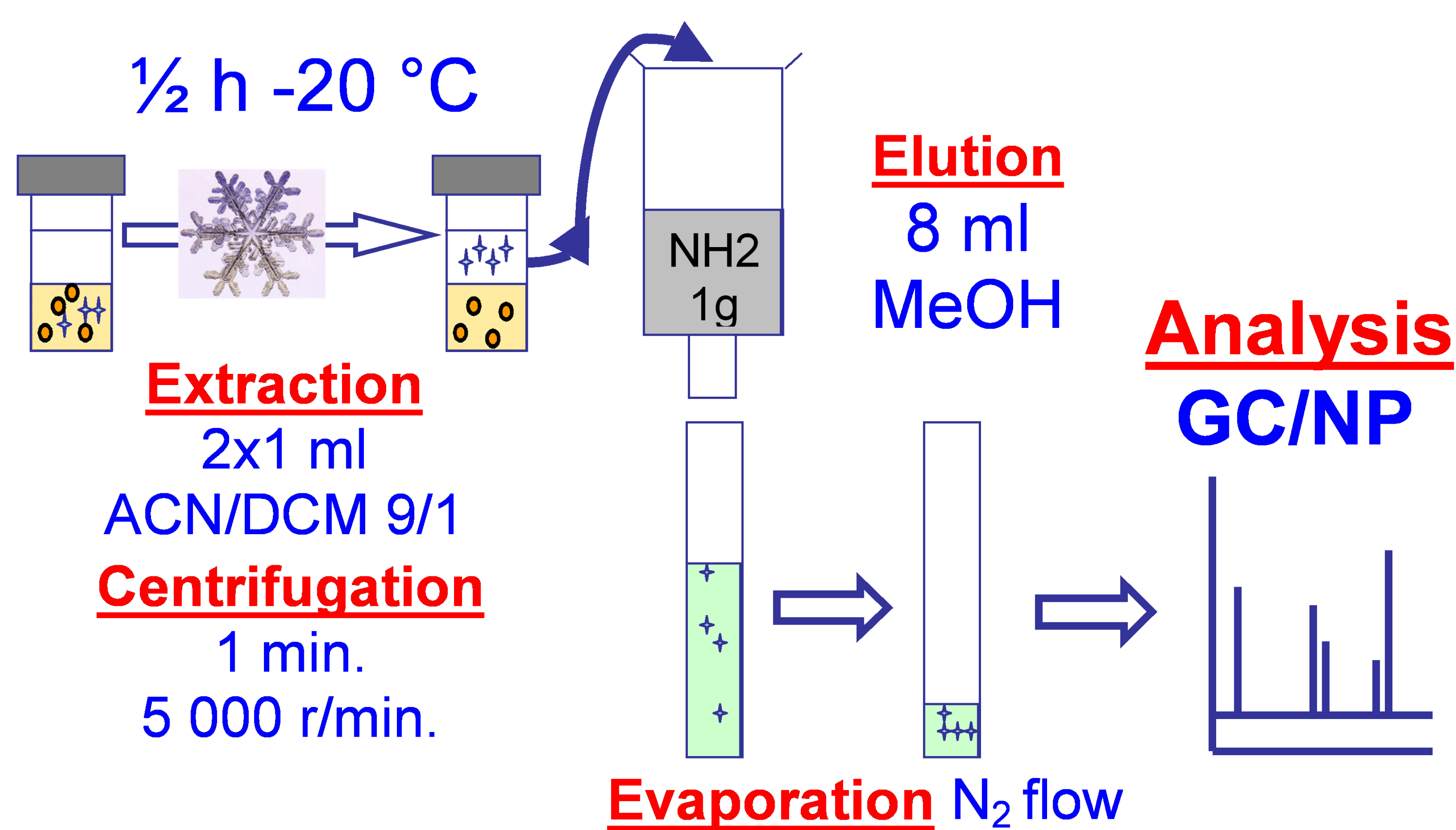


Figure 1: analytical diagram

Operating conditions

Weigh to the nearest 1 mg about 200 mg of sample into a 2ml vial. Add 1 ml of solvent mixture (acetonitrile/dichloromethane 90/10). Shake the vial 30 sec. with Vortex, then centrifuge 1 min. (5 000 rounds/min.).

Let the vial ½ h at -20°C.

Put the extract on an aminopropyl cartridge (1g, conditioned with 5 ml hexane then 2 ml methanol) without eluting.

Repeat the extraction once.

Elute the extracts in a 10 ml conical tube, then add 8 ml of methanol on the cartridge and elute in the same conical tube.

Add 500 µl toluene in the conical tube and evaporate solvents to 50 µl under a nitrogen flow using a water bath at 30°C. Add 50 µl of internal standard solution (heptenophos, 1280 ng/ml).

Complete the volume to 1 ml with injection solvent (isooctane).

Apparatus

GC/NPD : Varian Star 3400 CX.

Column : DB 1701, 14% cyanopropyl-phenyl, 86% méthylpolysiloxane, 30 m, Ø 0,32 mm, 0,25 µm. Progr. T° : 80°C (5 min.), 6°C/min. to 270°C, 270°C (20 min). Inj. : 80°C (0,5 min.), 250°C/min. to 250°C, 250°C (55 min.) T° detector : NPD, 300°C

Validation

Linearity

Linearity was verified for 13 OPP in the range 5-2000 ng/ml corresponding to 20-10 000 µg/kg in sample.

Repeatability and reproducibility

Repeatability and reproducibility were evaluated using a sample spiked with 250 µg/kg of each pesticide. Repeatability assays were performed by the same operator the same day. Reproducibility assays were performed by two different operators, during two different days (table 1).

Limits of detection and quantification (table 1)

Limits of detection was determined as signal/noise = 3.

Limits of detection was determined as signal/noise = 9.

Pesticide	LOD mg/kg	LOQ mg/kg	RSD repeatability n=10	RSD reproducibility n=5
dichlorvos	0,01	0,03	11%	16%
diazinon	0,01	0,03	4%	3%
etrimfos	0,02	0,06	4%	4%
chlorpyrifos methyl	0,01	0,03	4%	7%
pyrimiphos methyl	0,01	0,03	4%	9%
chlorpyrifos ethyl	0,01	0,03	7%	7%
malathion	0,01	0,03	3%	4%
fenitrothion	0,01	0,03	5%	4%
parathion ethyl	0,01	0,03	7%	8%
methidathion	0,01	0,03	4%	2%
carbophenothion	0,01	0,03	5%	19%
azinphos methyl	0,01	0,03	4%	6%
azinphos ethyl	0,01	0,03	7%	10%

LOD: limit of detection, LOQ: limit of quantification, RSD: relative standard deviation

Table 1: List of pesticides determined, Limits of detection and quantification, repeatability, reproducibility

Trueness

Trueness was evaluated by the determination of recoveries at four levels of concentration (figure 2). Recoveries are in the range 70%-110% for all pesticides excepted dichlorvos (40%).

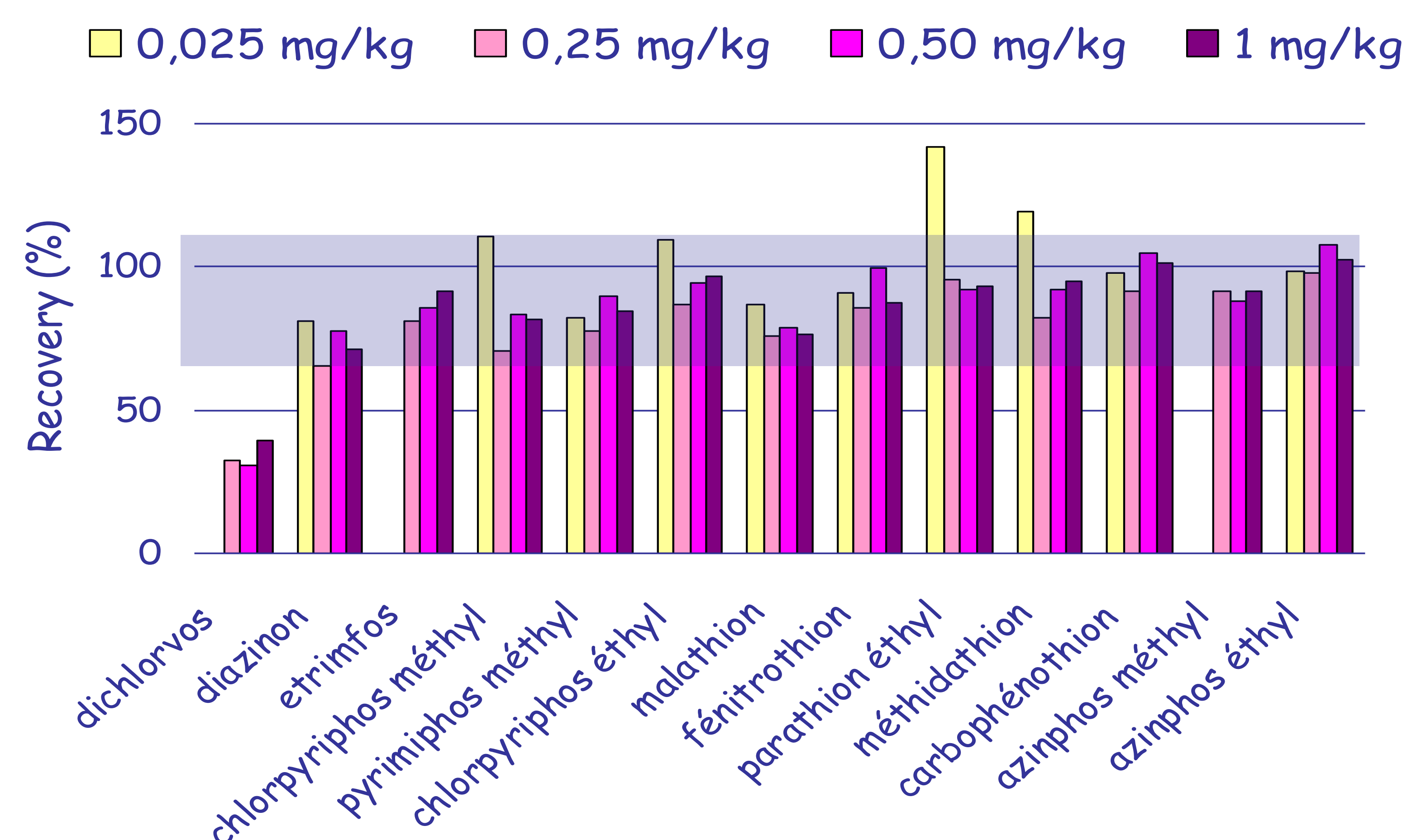


Figure 2: Recoveries

Robustness

The parameters chosen for the study of robustness were : test portion, solvents proportion, volume of extraction and volume of elution. Two were found critical : the **volume of extraction** and the **test portion**. Slight variations of these parameters induce significant variations on results.

Conclusion

A fast and simple method was developed for the analysis of 12 OPP in deo-distillates obtained by physical refining. Its principle is an extraction liquid/liquid followed by a clean-up on an aminopropyl cartridge.

The method was validated for 11 OPP. Linearity, trueness, repeatability, reproducibility and robustness were evaluated.