VALIDATION OF METHOD FOR ORGANOCHLORIDE PESTICIDES IN WATER BY GC/µECD AND GC/MS

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INTRODUCTION

The existing hydric resources in URUGUAY are widespread, having a very good availability of such in quality and amount.
Their uses are for: human supplying, irrigation, industry, cattle activity, agriculture, thermal tourism, recreation, spill of efluents, waste waters, hydroelectricity, among others.
Uruguay has as an economical, cultural and social goal, to distinguish itself in the context of the Nations as a "Natural Country". One of the most important environmental principles of our country is prevention and precaution. It is really advisable to avoid the production of environmental damages and also to adopt actions opposite to the imminence of serious and irreversible environmental damage and the human health. Aligned to this philosophy it is that Uruguay ratified the Agreement of Stockholm on Persistent Organic Pollutants (POPs).
Our institution has been working for 40 years in these subjects aligned to the environmental principles of the country, and to the national and international existing norms,
Knowing the importance that the results emitted by us could be internationally comparable and accepted, we decided to work for the accreditation of organochlorine pesticides (Lindane, Heptachlor and Aldrin) in different types of waters. Until this moment the technique is accredited by an internationally recognized organism such as UKAS (United Kingdom Accreditation System).

OBJETIVE

The purpose of this work is to show the validation of an analytical method for the simultaneous determination of three organochlorine pesticides: Lindane, Heptachlor and Aldrin in potable waters, underground waters and superficial waters. The validation involves the determination of the following parameters: accuracy , precision, limits of detection and quantification, selectivity, range of work, linearity curve, ruggedness and uncertainty.

EXPERIMENTAL PROCEDURE

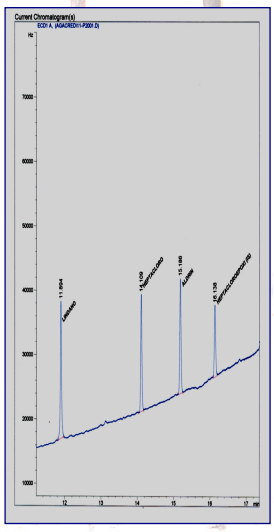
Test portion
1L water

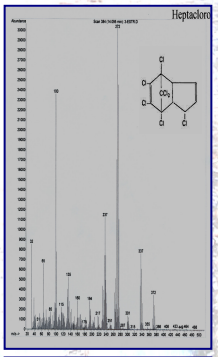
EXTRACTION
3 extractions with 100 mL hexane each

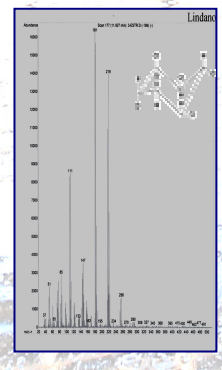
DRYING
Drying of the extract with sodium sulfate

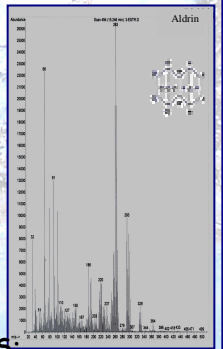
CONCENTRATION
Concentration of the extract with rotary evaporator
caution: avoid the extract into dryness

ANALYSIS
Analysis by HRGC-uECD and/or HRGC-MS









HRGC-µECD conditions:
Gas Chromatograph: HP 6890
Inlet: temperature 240°C and injection volume 1µL
Oven rate: 40°C 50°C/min
180°C(2.80min) 10°C/min
230°C(7.80min) 5°C/min
280°C(22min)
Mode injection: splitless
Detector: µECD
Column: HP1(50m × 200 µm × 0.50 µm)
Flow: 1.3 mL/min

HRGC-MS conditions:
Gas Chromatograph: HP 6890
Inlet: temperature 250°C and injection volume 1µL
Oven rate: 40°C (1min) 35°C/min
150°C() 5°C/min 240°C(10min)
Mode injection: splitless
Detector: MS
Source Masa temperature: 200°C
Interface temperature: 250°C
Column: HP5-MS(30m × 250 µm × 0.25 µm)
Flow: 1.0 mL/min

RESULTS & DISCUSSION

PRECISION
We worked with duplicates and a quality chart constructed with this duplicates. The target is that the difference of the duplicates must be between the control limits.

ACCURACY: we use as a measure of accuracy the recovery from spiked samples. We analyzed fortified samples at different levels by duplicate (3 different levels), with different analysts (three analysts), with blank samples and targets of reagents. Recovery mean: for Lindane 77%, for Heptachlor 76% and for Aldrin 71%.

DETECTION LIMIT (DL) and QUANTITATION LIMIT(QL):
DL: We spike a blank sample at the lowest detectable amount. This amount is bigger than 3 signal/noise.
QL: We considered the lowest concentration of the calibration curve as QL.

SPECIFICITY: The blank sample has no interfering peaks at retention time of the studied pesticides. Confirmation by GC/MS/EI.

LINEARITY: We constructed a linear curve with 10 points. The linear interval for Lindane, Heptachlor and Aldrin is 0.0004 -0,07 ug/L (uECD) and 0,001- 0,07 ug/L (MS) with $r^2 \geq 0.997$.

RUGGEDNESS: We study a critical point of the analytical technique: the degradation of the compounds when taking the extract into dryness. We measured the degradation of the compounds varying the time we left the extract once it was dry (5, 15 and 30 minutes). Degradation of Lindane: 22, 23 and 41 % as time increase. For heptachlore: 39, 39 and 73 % and for aldrin: 13, 16 and 49%.

UNCERTAINTY: The calculation is based in Eurachem Guide.. The expanded uncertainty for Lindane, Heptachlor and Aldrin is of 23%.

CONCLUTIONS:

The validated method is adequate for the determination of these organochlorine pesticides because our results are satisfactory and within the criteria of conformity determined by the standing norms. Our intention is to continue demonstrating the quality of our analytical results, extending the accreditation to other organochlorine pesticides in waters, other environmental matrices (grounds and sediments) and in foods.

REFERENCES:

Norma Española UNE-EN ISO 6468 junio **1997**
Quality Control Procedures for Pesticide Residues Analysis SANCO/10232/**2006**
Eurachem Guide

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*Imagen: Represa de Canelón Grande. Canelones - Uruguay