# Pesticide residue determination in common bean using QuEChERS approach and GC-MS/MS analysis

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## INTRODUCTION

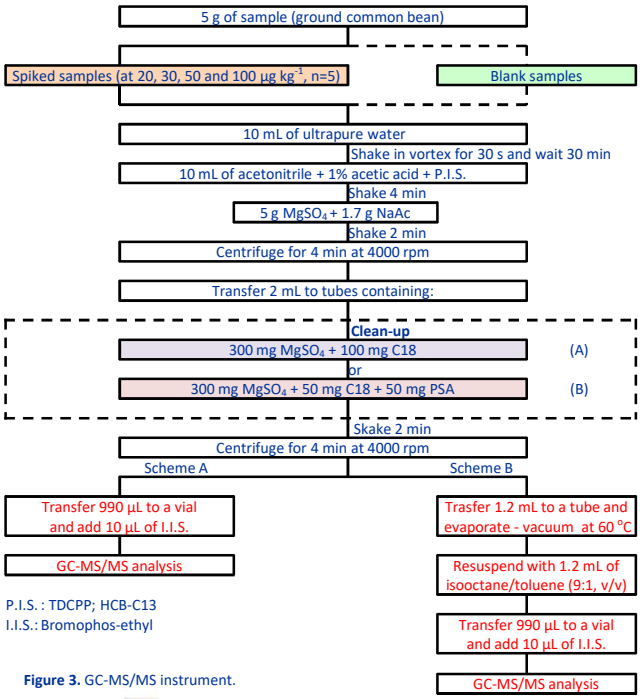
The global importance of common bean *(Phaseolus vulgaris* L.) cannot be underestimated, it is a staple food in Latin American countries (especially in Brazil) and Africa, accounting for approximately 50% and 25% of the world's consumption in volume, respectively. In Brazil, common bean is a daily lunch dish, consumed mixed with rice and as a traditional dish known as "feijoada". The common bean is rich in high-quality protein, carbohydrates, fiber and micronutrients especially iron, zinc, thiamine, folic acid and pro-vitamin A. Its consumption is relatively high specially among needy people, precisely because of the lower price in comparison to animal protein sources and it is associated with health improvement as potentially disease-preventing and health-promoting compounds. Despite its importance worldwide, studies about contamination of common bean with pesticides are rarely reported in literature. So, the goals of this study were to optimize and validate a multiresidue method and apply it in monitoring of pesticides contamination in common bean samples from Brazil (REICHERT, 2020).

## EXPERIMENTAL CONDITIONS

**Figure 1.** Sample processing.


Optimization of QuEChERS approach involved evaluation of two clean-up sorbents (PSA and $C_{18}$) and need or not of solvent exchange before GC-MS/MS analysis.

**Figure 2.** Scheme of the QuEChERS approach evaluated for the ground common bean samples.




P.I.S. : TDCPP; HCB-C13
I.I.S.: Bromophos-ethyl

**Figure 3.** GC-MS/MS instrument.

**Figure 4.** Common bean samples.

**Chromatographic Conditions**

- Injection volume: 5 µL, split ratio 1:5.
- Injector: 1079 PTV/LVI.
- Capillary column: VF-5 MS (30 m x 0.25 mm i.d. x 0.25 µm film).
- Oven temperature program: 80 °C (1.0 min), up to 180 °C at 25 °C $min^{-1}$, then to 280 ºC at 10 °C $min^{-1}$, and finally to 300 °C at 30 °C $min^{-1}$ (1 min).
- Injector temperature: 80 °C (0.1 min), then ramped up to 300 °C at 200 °C $min^{-1}$.
- Mobile phase (He): 1.0 mL $min^{-1}$.

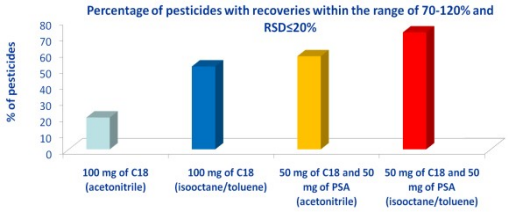
**Mass spectrometry conditions:**

- Ionization mode: EI.
- Transferline temperature: 280 °C.
- Ion source temperature: 250 °C.
- Acquisition mode: MRM.

## RESULTS

### Preliminary tests for method optimization

**Figure 5.** Percentage of pesticides with recoveries from 70–120% and RSD ≤20% (for the spike concentration of 100 µg $kg^{-1}$) according to the clean-up sorbents evaluated and solvent of the injected extract.




The best results were obtained using C18 and PSA for clean-up followed by solvent exchange before GC-MS/MS analysis. Thus, this extraction scheme was selected for method validation.

### Validation study

**Table 1.** Validated pesticides and limits of quantification (LOQ) established according to the lowest spike concentration that provided recoveries from 70-120% and RSD ≤ 20% in accuracy tests (calculated from 5 replicate samples).

| Pesticide | LOQ (µg $kg^{-1}$) | Pesticide | LOQ (µg $kg^{-1}$) | Pesticide | LOQ (µg $kg^{-1}$) | Pesticide | LOQ (µg $kg^{-1}$) | Pesticide | LOQ (µg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| Acetochlor | n.d. | DDD 4,4 and DDT 2,4 | 20 | Fenoxycarb | n.f.r. | Methiocarb | 100 | Prothiofos | 20 |
| Acrinathrin | 100 | DDE 2,4 | 30 | Fenpropathrin | n.f.r. | Mevinphos-cis | n.f.r. | Pyraclostrobin | n.f.r. |
| Alachlor | 30 | DDE 4,4 | 30 | Fenpropidin | 100 | Mirex | n.d. | Pyrazophos | 100 |
| Aldrin | 100 | DDT 4,4 | 20 | Fenpropimorph | 20 | Myclobutanil | 30 | Pyridaben | 30 |
| Allethrin I-II | 50 | Deltamethrin | n.d. | Fenthion | 100 | Oxadiayl | 30 | Pyridaphenthion | 30 |
| Azinphos-ethyl | 100 | Dichloran | n.f.r. | Fenvalerate | n.f.r. | Oxyfluofen | n.f.r. | Pyrifenox (E-) | n.f.r. |
| Azinphos-methyl | n.f.r. | Dichlorvos | n.d. | Fipronil | 100 | Parathion-ethyl | 50 | Pyrifenox (Z-) | n.f.r. |
| Azoxystrobin | n.f.r. | Dichlorobenzophenone-4,4 | 100 | Fludioxonil | n.f.r. | Parathion-methyl | 30 | Pyrimethanil | n.f.r. |
| Bifenazate | n.f.r. | Dieldrin | 100 | Fluquinoconazole | 100 | Pencycuron | 50 | Pyriproxyfen | 30 |
| Bifenthrin | 20 | Diethofencarb | 50 | Flusilazole | n.f.r. | Pendimethalin | 100 | Quinalphos | 50 |
| Bitertanol I-II | 100 | Difenoconazole I-II | n.f.r. | Flutolanil | 20 | Permethrin-cis | 50 | Quinoxyfen | 50 |
| Boscalid | 20 | Dimethomorph | n.f.r. | Fluvalinate I-II | 30 | Permethrin-trans | n.d. | Quintozene | n.f.r. |
| Bromuconazole I | n.f.r. | Diniconazole | 30 | Folpet | n.d. | Phenthoate | 50 | Tebuconazole | 100 |
| Bromuconazole II | n.f.r. | Diphenylamine | n.d. | HCH-alpha | n.f.r. | Phenylphenol-2 | n.d. | Tebufenpyrad | 20 |
| Bupirimate | 50 | EPN | 100 | HCH-beta | 100 | Phosalone | 20 | Tetraconazole | 50 |
| Buprofezin | n.f.r. | Endosulfan-alfa | n.f.r. | HCH-gamma | n.d. | Phosmet | 100 | Tetradifon | n.f.r. |
| Cadusofos | 100 | Endosulfan-beta | n.d. | Haloxyfop-2-ethoxyethyl | 30 | Phthalimide | n.f.r. | Tetrahydrophthalimide | n.d. |
| Captan | n.d. | Endosulfan-sulfate | 100 | Heptachlor | 20 | Picoxystrobin | 30 | Tetramethrin I-II | 30 |
| Carbaryl | n.f.r. | Endrin | n.f.r. | Heptochlor-epoxide | 100 | Piperonyl-butoxide | 20 | Tolcofos-methyl | 50 |
| Carbofuran | 100 | Epoxiconazole I-II | 20 | Hexachlorobenzene | n.f.r. | Pirimiphos-ethyl | 50 | Transfluthrin | n.f.r. |
| Carboxin | n.f.r. | Ethion | 50 | Hexaconazole | n.f.r. | Pirimiphos-methyl | 50 | Triadimefon | 100 |
| Chlorfenvinphos | 20 | Ethofenprox | 20 | Indoxacarb | n.f.r. | Procymidone | 20 | Triadimenol I-II | 30 |
| Chlorpyrifos-ethyl | 20 | Ethoprophos | 100 | Isoprothiolane | 50 | Profenofos | 20 | Triazophos | 50 |
| Cyfenothrin I-III | 100 | Fenamidone | 100 | Kresoxim-methyl | 50 | Prometryn | 30 | Trifloxystrobin | 100 |
| Cyfluthrin I-IV | 100 | Fenarimol | 50 | Malathion | 20 | Propargite I-II | n.f.r. | Trifluralin | n.d. |
| Cyhalothrin-lambda | 50 | Fenazaquin | 30 | Mephosfolan | n.f.r. | Propham | n.f.r. | Vinchlozolin | 100 |
| Cypermethrin I-IV | 50 | Fenbuconazole | 50 | Mepronil | 100 | Propiconazole I-II | 100 | Zoxamide | 100 |
| Cyproconazole I-II | 100 | Fenhexamid | n.f.r. | Metalaxyl | 100 | Propoxur | 100 | | |
| DDD 2,4 | 20 | Fenitrothion | 100 | Methidathion | n.d. | Propyzamide | n.f.r. | | |

n.d.: not detected; n.f.r.: not fulfilling requirements for quantitative method, due to recoveries outside range of 70–120% or RSD > 20%.

From the 142 compounds analysed (139 pesticides and 3 degradation products), 91 compounds (64.1%) were successfully validated (90 pesticides and dichlorobenzophenone-4,4, the degradation products of dicofol). Matrix effects were present (>20%) for 78.9% of the pesticides and mainly positive (enhancement), so quantifications were done via matrix matched standards to avoid inaccurate results.

**Figure 6.** Linearity of the analytical curves.

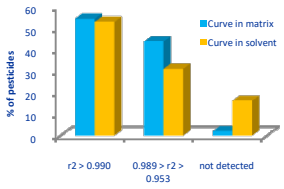



**Figure 7.** Total ion chromatogram showing the selectivity of the method.

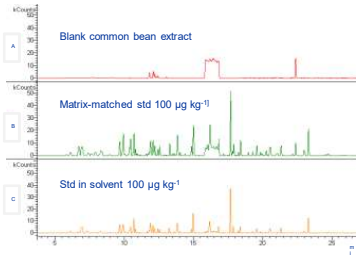
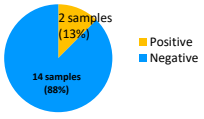



**Figure 8.** Results of sample analysis.




- A total of 16 common bean samples were analysed.
- Two samples were positive.
- Tebuconazole was detected in one sample at a concentration below the MRL (100 µg $kg^{-1}$) in Brazil.
- A second samples was positive for picoxystrobin, permethrin and cyproconazole. Cyproconazole is not allowed for the crop consisting of a violation. For picoxystribin and permethrin, unfortunately it was not possible to quantify because they were detected at a concentration below the method LOQ.

## CONCLUSIONS

- An analytical method was successfully validated for determination of 90 pesticides and one pesticide degradation product (dichlorobenzophenone-4,4[b]) in common bean.
- QuEChERS optimization study demonstrated that the combination of C18 and PSA for clean-up followed by a solvent exchange step before GC-MS/MS analysis was able to provide important advantages in terms of recoveries of the pesticides.
- The LOQs of the pesticides were ≤ than the maximum residue limits (MRL) set by the Brazilian low for almost all the pesticides.
- Sixteen common bean samples from Southern Brazil were analyzed and two were positive. The presence of cyproconazole in one sample consists of o violation and shows that the control of pesticide residues in common bean is important to ensure compliance with the MRL and to ensure food safety.

## REFERENCE

REICHERT, B. et al. *J Sci Food Agric*, v. 100, 2425–2434, 2020.

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