DITHIOCARBAMATE DETERMINATION IN YERBA MATE (*Ilex paraguariensis*) PRODUCED IN BRAZIL BY GC-MS

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INTRODUCTION

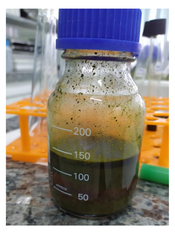
Ilex paraguariensis, known as yerba mate, originating of South America is an important commercial product in Latin America. Yerba Mate has become popular worldwide over the years due to many pharmacological properties as great antioxidant capacity, antiinflammatory, antiproliferative, antimutagenic and antiobesity properties, besides this might contribute to preventing the development of cancer and cardiovascular diseases.

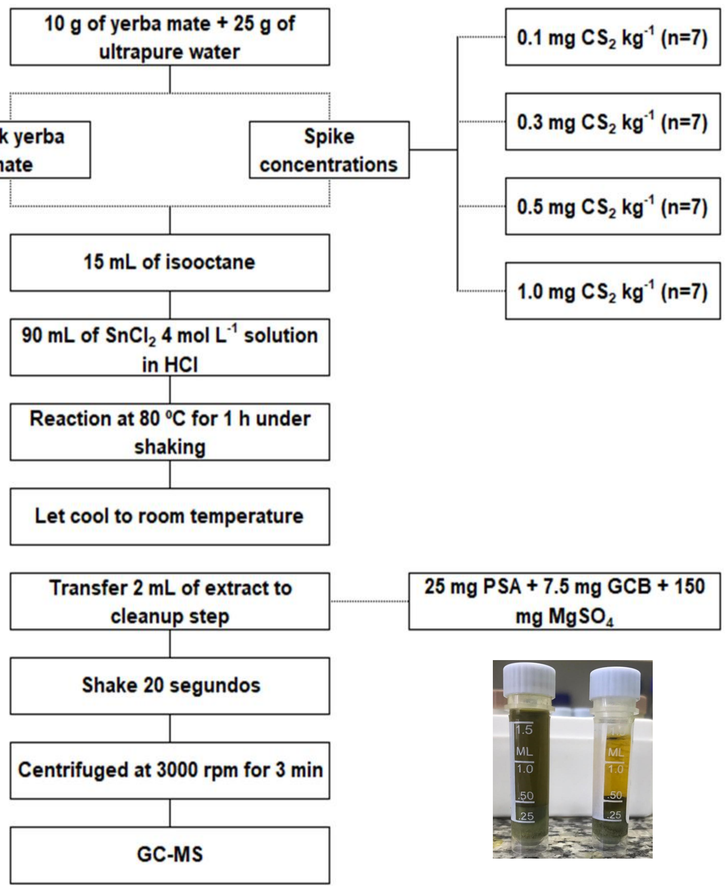
In Brazil, there are no authorized pesticides for the cultivation of yerba mate. However chemical control for most pesticides is carried out according to recommendations for other crops. Among pesticides popularly used are fungicides such as captan and dithiocarbamate.

The aim of this work was to optimize and validate an analytical method for determine dithiocarbamates from several commercial yerba mate produced in different municipalities of Rio Grande do Sul state, in Brazilian southern region.

EXPERIMENTAL

EXTRACTION METHOD PROCEDURE





INSTRUMENTAL CONDITIONS

Cromatographic conditions

- **Capillary column:** ZB-5 MS (30 m x 0.25 mm I.D. x 0.25 µm)
- **Injection volume**: 1 µL, split mode 1:10
- **Injector temperature:** 250 °C
- **Oven temperature program:** ramp started at 40 °C (1.8 min), rising to 240 ºC at 50 ºC min^{-1} (2 min)
- **Mobile phase (He):** 1.0 mL min^{-1}

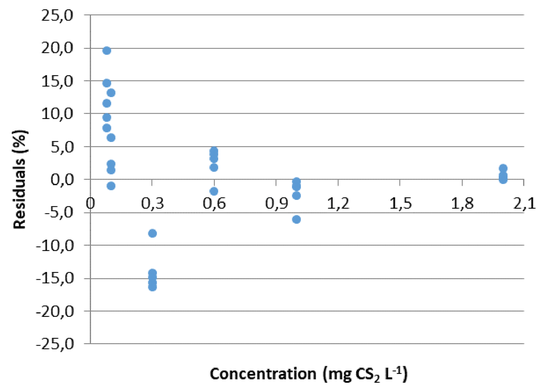
Mass spectrometry conditions

- **Ionization mode:** SIM (Selected Ion Monitoring)
- **Ion transition:** 76 and 78 m/z
- **Transferline temperature:** 200 °C
- **Ion source temperature:** 230 °C

RESULTS

Yerba mate linearity was assessed by repeated injections (n=7) of analytical solutions at the concentrations of 0.08, 0.1, 0.3, 0.6, 1.0 and 2.0 µg CS_2 mL^{-1} prepared in organic solvent (Isooctane) and in Yerba mate extract (matrix-matched calibration standard solutions). The calibration curves were linear with correlation coefficients r2> 0.99. The deviation of the back-calculated concentrations of the calibration standards solutions from the true concentrations is in the range of ± 20%.

Figure 1. Deviation of back-calculated concentrations (”residuals”) of the individual standard concentrations, obtained from using the analytical curve from standard solutions prepared in blank yerba mate extract using GC-MS.



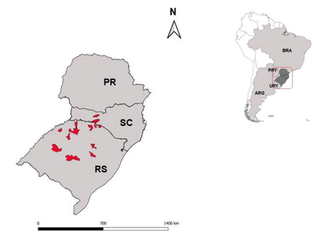
The LOD and LOQ were established at 0.1 and 0.3 mg CS_2 kg^{-1}, respectively.

Matrix effects was low (-5,1) indicating that cleanup was efficient to remove interferences from the extract.

Table 1. Average recoveries, precision (RSDr) and intermediate precision (RSDR) obtained for yerba mate spiked with thiram at 0.1, 0.3, 0.5 and 1.0 mg CS_2 kg^{-1} equivalent concentrations. Two analysts using GC-MS performed analyses.

Spike concentration (mg CS_2 kg^{-1})	Analyst 1		Analyst 2		Average		p-value
	Recovery (%) (n= 7)	RSDr (%)	Recovery (%) (n= 7)	RSDr (%)	Recovery (%) (n= 14)	RSDR (%)	
0.1	118.2	5.3	83.4	9.5	100.8	19.4	< 0.0001
0.3	98.9	11.2	86.4	8.1	92.5	11.4	0.03
0.5	93.0	6.8	96.0	5.0	94.5	5.8	0.20
1.0	73.1	4.5	71.3	5.7	72.2	5.1	0.51

The validated method was applied to 20 samples of yerba mate grown in the main producing cities in Rio Grande do Sul state. The quality of the yerba mate was satisfactory, in terms of the presence of dithiocarbamate, because no resides was found in the analyzed samples.



CONCLUSION

The method for dithiocarbamate analysis by GC-MS met the SANTE validation criteria and showed reliable results for analysis of real samples. Although there is no MRL for dithiocarbamate in yerba mate, the method presented, is remarkably selective and accurate down to a quantification level of 0.3 µg kg^{-1} .

Therefore, this study for determining dithiocarbamates is of great importance in order to ensure that this processed product is safe for the consumer.

Acknowledgments: CAPES, CNPq, MCTI, MAPA and UFSM