



Development of a Simplified Sample Preparation Method for the Determination of Paraquat and Diquat in Food Commodities

Diana Inês Ströher Kolberg, Dorothea Mack, Michelangelo Anastassiades

Chemisches und Veterinäruntersuchungsamt Stuttgart, Schaflandstr. 3/2, 70736 Fellbach, Germany

Introduction

Quaternary ammonium compounds constitute an important group of pesticides. Paraquat and diquat are non-selective contact herbicides used among others on cereals as desiccants and on potatoes for defoliation to facilitate mechanical harvest. Their physical properties, such as the low vapor pressure, high water solubility and the high binding potential to soil which prevents their leaching to aquifers and their uptake by crop plants, make them suitable for agricultural uses. Due to the permanent ionic character, these herbicides are highly hydrophilic and thus not amenable to multiresidue methods involving liquid-liquid-partitioning. At the same time their high affinity to binding on various surfaces requires special attention in extraction as well as the storage of solutions. Within this project the extraction efficiency of these two compounds from potatoes and barley was tested at various conditions. The method was tested on spiked barley and potato samples as well as on samples containing incurred paraquat and diquat.

Experimental Procedure

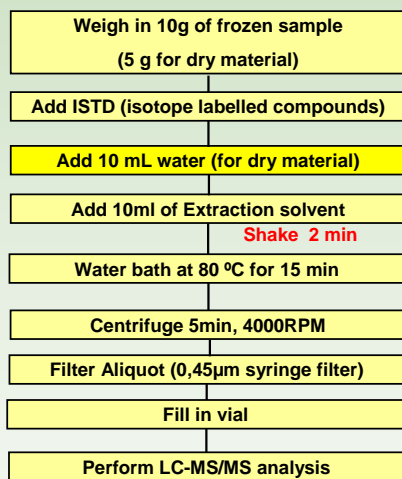


Figure 1: Procedure with different extraction solvents

Extraction Solvents

- 45% MeOH+50% Water+5% FA
- Water + 2% Formic Acid
- MeOH + 5% Formic Acid
- MeOH + HCl 0,1M (1:1)
- MeOH + H₂SO₄ 0,1M (1:1)

Besides the different extraction solvents, we did also evaluate the effect of shaking time (2 - 30 min) without heating, as well as the heating time itself. Extractions using sulfuric acid 0,6 N (commonly used in previous methods including industry methods) were also tested with the heating time ranging between 30 min and 5h at 100 °C without any improvement compared to the present method.

Conclusion

The procedure established for diquat and paraquat involves extraction with MeOH + HCl 0,1M (1:1) at 80°C for 15 minutes. Analysis is performed by LC-MS/MS using the isotopically labelled compounds as ISTDs with the ISTDs helping to effectively eliminate errors caused by matrix-induced suppression in LC-MS/MS. The recoveries achieved were in the range of 92 – 114% for all tested compounds/ commodity/ spike level combinations. The good sensitivity of the method (LOQ 0,006 mg/kg), and the excellent recoveries and RSDs demonstrate that the method is suitable for routine analysis of these herbicides. Although much simpler, the extraction procedure led to extraction efficiencies that are comparable to those of previously published more tedious methods (incurred residues of paraquat and diquat in potato and barley samples).

LC-MS/MS - Conditions

Column Obelisc R 2.1 x 150mm

Pre-column Obelisc R 2.1 x 10mm

Eluent A 20 mmol NH₄-formate in water pH 3 adjusted with formic acid

Eluent B Acetonitrile

Injection Volume 10 µL

Flow rate 0,4 mL min⁻¹

Transition masses (m/z):

Paraquat (186/171, 171/77, 171/155, 171/103, 186/155); Paraquat D6 (192/174)

Diquat (184/128, 183/157, 184/156, 184/78, 183/130); Diquat D4 (188/160)

Results

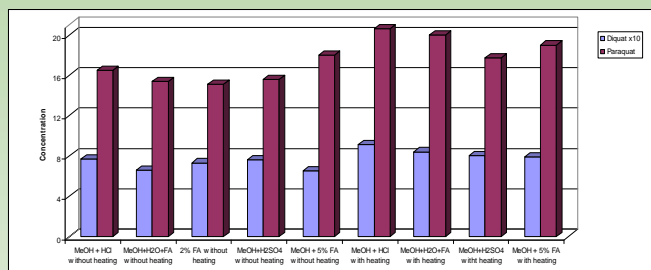


Figure 2: Comparison of the different extraction solvents on incurred wheat sample (n= 3)

* The extraction with water + 2% formic acid generated a viscous suspension upon heating and was discarded

	Potato				Barley			
	0,01 mg/kg		0,1 mg/kg		0,01 mg/kg		0,1 mg/kg	
	Rec	RSD	Rec	RSD	Rec	RSD	Rec	RSD
Diquat	101	2,4	101	4,4	100	1,7	100	3,1
Paraquat	111	5,6	105	1,4	92	7,0	114	4,3

Table 1: Recoveries and RSDs obtained for diquat and paraquat spiked on potato and barley

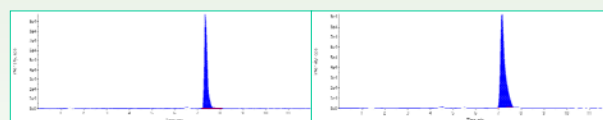


Figure 3: MRM chromatograms of diquat and paraquat in potato at spike level 0,01 mg/kg using instrument API 5500

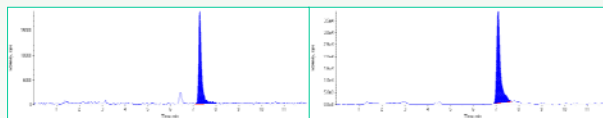


Figure 4: MRM chromatograms of diquat and paraquat in barley at spike level 0,01 mg/kg using instrument API 5500