Methods to Analyze Glyphosate (GLY) and Its Main Degradation Product Aminomethylphosphonic Acid (AMPA) in Grains and Grain-Based Foods

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This report provides a list of methods for the analysis of glyphosate (GLY) and aminomethylphosphonic acid (AMPA) published in peer-reviewed scientific literature (Table I). It is not meant to be an exhaustive list of testing methodologies, but to indicate the breadth of technologies used, range of sensitivity, range of matrices, and range of validation status. Preference for inclusion on this list is given to more recent publications as they reflect technologies and materials currently available and also reference older work. These are mature methods using common technologies that have been validated and applied to real samples, as opposed to methods under development.

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Table I. Published methods for analyzing glyphosate (GLY) and aminomethylphosphonic acid (AMPA) in grains and grain-based foods[a]

Applicable Matrices	Validation Status	Detection Technology	Sample Preparation	Reported Sensitivity	Reference
Corn	Collaborative validation study	GC-MS	Extraction with water; cation exchange cleanup; derivatization	GLY LOQ = 0.05 mg/kg	Alferness and Wiebe (1)
Barley, lentils, malt, whole oats, wheat	Single laboratory validation	ELISA	Extraction with 1 N HCl	GLY LOQ = 0.3 mg/kg	Tittlemier et al. (13)
Oats, soybean	Single laboratory validation	HILIC-MS/MS	Extraction with water, formic acid, and methanol	GLY LOQ = 0.1 – 0.5 mg/kg AMPA LOQ = 0.05 mg/kg	Herrera López et al. (5)
Corn, rice	Single laboratory validation	IC-MS/MS	Extraction with water, formic acid, and methanol	GLY LOQ = 0.01 mg/kg	Santillo et al. (12)
Barley, corn, rice, wheat	Single laboratory validation	LC-MS/MS	Extraction with water, methanol, and dichloromethane; derivatization with FMOC-Cl	GLY LOQ = 0.005 mg/kg	Liao et al. (6)
Barley, lentils, malt, whole oats, wheat	Single laboratory validation	LC-MS/MS	Extraction with water and dichloromethane; derivatization with FMOC-Cl; SPE	GLY LOQ = 0.05 – 0.1 mg/kg AMPA LOQ = 0.05 – 0.2 mg/kg	Tittlemier et al. (13)
Corn, soybean	Single laboratory validation	LC-MS/MS	Extraction with water, formic acid, and dichloromethane; derivatization with FMOC-Cl; SPE	GLY LOQ = 0.0005 – 0.002 mg/kg AMPA LOQ = 0.0005 – 0.002 mg/kg	Oulkar et al. (10)
Corn, soybean	Single laboratory validation	LC-MS/MS	Extraction with 50 mM acetic acid/ 10 mM Na_2EDTA; SPE	GLY LOQ = 0.05 mg/kg AMPA LOQ = 0.05 mg/kg	Chamkasem and Harmon (2)
Soybean-based infant formula	Single laboratory validation	IC-FLD	Extraction with 0.1 M HCl; ion exchange column cleanup; post-column derivatization	GLY LOQ = 0.02 mg/kg AMPA LOQ = 0.02 mg/kg	Rodrigues and de Souza (11)
Wheat flour	Single laboratory validation	Flow injection-MS/MS	Extraction with water	GLY LOQ = 0.3 mg/kg[b]	Mol and van Dam (8)
Oat flour, rye flour, wheat flour	Single laboratory validation	LC-MS/MS	Extraction with water, methanol, and dichloromethane; derivatization with FMOC-Cl	GLY LOQ = 0.02 mg/kg AMPA LOQ = 0.02 mg/kg	Goscinny et al. (3)
Soybean	Single laboratory validation	LC-MS/MS	Extraction with water and dichloromethane; protein precipitation	GLY LOQ = 0.3 mg/kg AMPA LOQ = 0.3 mg/kg	Martins-Júnior et al. (7)
Wheat	Single laboratory validation	IC-MS/MS	Extraction with water; in-line reverse-phase column cleanup	GLY LOQ = 0.06 mg/kg[b]	Granby et al. (4)
Beer, corn, malt	Minimal	IC-MS/MS	Extraction with water (grains); sequential cation and anion exchange SPE	GLY LOQ = 0.01 mg/kg AMPA LOQ = 0.01 mg/kg	Nagatomi et al. (9)

[a] GC-MS: gas chromatography–mass spectrometry; LOQ: limit of quantitation; ELISA: enzyme-linked immunosorbent assay; HILIC-MS/MS: hydrophilic-interaction liquid chromatography–tandem mass spectrometry; IC-MS/MS: ion chromatography–tandem mass spectrometry; LC-MS/MS: liquid chromatography–tandem mass spectrometry; IC-FLD: ion chromatography with fluorescence detection.

[b] Estimated as 3× reported limit of detection.