Chapter 34
Determination of Veterinary Pharmaceuticals Residue in Soil and Biological Materials: A Review of Current Analytical Methods

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Abstract Veterinary pharmaceuticals have been extensively used in animal husbandry for control of disease and growth promoters. These compounds are excreted from animals via urine and faeces, end up in the environment through untreated animal waste disposal. Veterinary pharmaceuticals often exist in the complex solid environmental samples such as manure, slurry, and soil which require extensive extraction, clean-up and analysis method. This review highlights the current analytical methods for the analysis of veterinary pharmaceuticals in complex solid environmental matrices, including soil, animal manures and sediment. The aim of this review is to compare and summarize the performance of each method in terms of recovery, method detection limit (MDL) and method quantification limit (MQL).

Keywords Review · Veterinary pharmaceuticals · Soil · Manure · Analytical methods

Highlights

- Pharmaceutical analysis in solid samples requires complex extraction method.
- MeOH:EDTA:McIlvaince buffer is frequently reported as extraction solvent for solids.

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A. Z. Aris et al. (eds.), *From Sources to Solution*,
DOI: 10.1007/978-981-4560-70-2_34,

- MeOH:ACN:0.1 M EDTA:McIlvaine extraction buffer is proposed to improve recovery.
- LC–MS/MS allows multi-residue, sensitive and selective pharmaceuticals analysis.
- HPLC–UV and HPLC-FLD are still being used due to its lower operating cost.

Introduction

All the while, the trends for analysis of pharmaceuticals in environment are focused in aqueous samples especially on human pharmaceuticals. Unlike human pharmaceuticals, veterinary pharmaceuticals often exist in the complex solid environmental samples such as manure, slurry, and soil. Very few studies have been devoted to pharmaceuticals in solid environmental samples due to pharmaceuticals being a large group of pollutants from different chemical classes with different physico–chemical properties (polar, semi polar, non polar, acidic, basic, neutral, strongly, moderately and weakly sorbed). In this review, we summarized the current available methods for determination of veterinary pharmaceuticals in soil and biological materials; the performance of each method is presented in Table 34.1.

Materials and Methods

Sample Preparation and Extraction

Ultrasonic extraction is known as a popular technique which is rapid and does not require large volumes of solvent or expensive instrumentation. This method has been successfully applied to pharmaceuticals extraction in solid environmental samples (Blackwell et al. 2004; Kim and Carlson 2007; Carballo et al. 2007; Aust et al. 2008; Karcı and Balcıoğlu 2009). MeOH: EDTA: McIlvaince buffer was frequently reported as extraction solvent for ultrasonication to extract antibiotics from soil and biosolids (Blackwell et al. 2004; Aust et al. 2008; Karcı and Balcıoğlu 2009). However, this extraction buffer limits to extract only high polarity compounds such as antibiotics whereas low polarity compounds such as hormones are often difficult to extract due to the strong partitioning affinity to soil and organic matter (Ho et al. 2012). Therefore, MeOH:ACN:0.1 M EDTA: McIlvaine buffer was proposed by Ho et al. (2012) to improve the recovery of low polarity analytes.

Table 34.1 Methods to determine veterinary pharmaceuticals in different sample matrices

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Trimethoprim	Soil,	Ultrasonication with ACN: MeOH: EDTA-McIlvaine buffer (pH 6)	Oasis HLB 3 cc/ 60 mg	HPLC	MS/MS	72–103 (S)	0.5–3 (S) 1–5 (M)	2–10 (S) 3–16 (M) 5–15 (C)	Ho et al. (2012)
Tilmicosin	Chicken manure,			Waters Xtera C18, 10.0 cm, 2.1 mm, 3.5 μm	ESI (+)	63–113 (M)	2–5 (C)		
Tylosin									
Erythromycin						63–119 (C)			
Enrofloxacin									
Flumequine	Compost								
Norfloxacin									
Sulfadiazine									
Doxycycline									
Progesterone									
Oxytetracycline	Poultry manure, cattle manure, soil	Ultrasonication with MeOH: EDTA-McIlvaine buffer (pH 6)	SAX 6 cc/ 500 mg,	HPLC	FLD	60–86 (S)	NR	NR	Karcı and Balcıoğlu (2009)
Chlortetracycline				50 × 4.0 mm, 3 μm, YMC-Pack ODS-AQ column	(360 nm)	62–77 (M)	NR	NR	
Suldiazine			Oasis HLB 6 cc/ 200 mg		FLD	69–101 (S)	NR	NR	
Sulfathiazole					(270 nm)				
Sulfamethoxazole						14–82 (M)			
Sullfachloropyridazine									
Ciprofolxacin					FLD	46–55 (S)	NR	NR	
Enrofloxacin					(280/ 450 nm)	24–42 (M)			

(continued)

Table 34.1 (continued)

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Sulfamethazine	Cattle manure, soil	Ultrasonication with MeOH: EDTA-McIlvaine buffer (pH 6)	SAX	HPLC	MS/MS	38–73 (S)	NR	5 (S/M)	Aust et al. (2008)
Chlortetracycline			6 cc/ 500 mg, Oasis HLB	Nucleosil 125 × 3.0 mm, 100–5 mm reversed-phase column	ESI(+)		NR	5 (S/M)	
Tylosin			6 cc/ 200 mg				NR	3 (S/M)	
Tetracycline	Pig slurry, chicken manure, turkeys manure, soil	Ultrasonication with EDTA McIlvaine	SPE Isolute C_{18}	HPLC	MS/MS	71–94 (M)	NR	1.2–22 (M)	Carballo et al. (2007)
Chlorteteracycline				Luna C_8 (150 × 2 mm, 5 μm)	ESI(+)	61–89 (S)		0.49–25 (S)	
Oxytetracycline									
Trimethoprim									
Sulfadimidine		Buffer (pH 4)							
Sulfadiazine									
Sulfathiazole									
Sulfamethozazole									
Sulfadoxine									
Ciprofloxacin					MS				
Enrofloxacin					ESI (+)				

(continued)

Table 34.1 (continued)

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Tetracycline Chlortetracycline Oxytetracycline Minocycline Demeclocycline Meclocycline Doxycycline Sulfathiazole Sulfamerazine Sulfamethazine Sulfachlorpyridazine Sulfamethoxazole Sulfadimethoxine Erythromycin Roxythromycin Tylosin Monensin Narasin Salinomycin	Sediment	Ultrasonication with McIlvaine Buffer with 5 % EDTA	Oasis HLB 3 cc/60 mg	HPLC 2.1 mm × 50 mm, 2.5 μm	MS/MS ESI (+)	12.6–113.2	0.3–3.6	NR	Kim and Carlson (2007)
Tylosin	Soil, pig slurry	Ultrasonication with MeOH: EDTA-McIlvaine buffer (soil)	SAX 6 cc/500 mg, Oasis HLB	HPLC GENESIS C_{18} 150 mm × 4.6 mm, 4 μm	FLD (285 nm)	86 ± 4 (S)	40 (S)	NR	Blackwell et al. (2004)
Oxytetracycline					FLD (355 nm)	102 ± 5 (M) 75 ± 3 (S)	18 (S) 70 (M)	NR	
Sulfachloropyridazine		Ultrasonication with EDTA McIlvaine Buffer (pig slurry)	6 cc/200 mg		FLD (285 nm)	89 ± 2 (M) 85 ± 4 (S)	18 (S) 140 (M)	NR	

ESI (+) electrospray ionization positive mode, *NR* not reported in the study, *S* soil, *M* manure, *C* compost

Instrumental Analysis

Liquid chromatography is widely used as a complementary technique to gas chromatography in residue analysis because of its applicability to the determination of polar, water soluble and non-volatile compounds without derivatization. UV detection (Blackwell et al. 2004; Hu et al. 2008; Karcı and Balcıoğlu 2009), and to a lesser extent mass spectrometry (Haller et al. 2002), and fluorescence detection (Blackwell et al. 2004; Karcı and Balcıoğlu 2009), have been used in the detection techniques in coupled to HPLC, for the analysis of pharmaceuticals in solid environmental samples.

Conclusion

The current available methods for determination of veterinary pharmaceuticals in soil and biological material are reviewed and summarized. In general, most of the extraction methods for veterinary pharmaceuticals in soil and biological materials require ultrasonic extraction with the aid of appropriate extraction buffer and subsequently analyzed by HPLC-FLD or LC–MS/MS.

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