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Various Analytical Methodologies for Determination of Selective α_{1A} Receptor Blocker Tamsulosin Hydrochloride and Its Combinations in Different Matrices

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Abstract Tamsulosin is a more selective α1A subtype antagonist, which maintains the α-antagonist effect on the prostatic capsule and bladder neck but has less of an effect on the vascular system and blood pressure. It has a better side effect profile than earlier α-adrenergic-receptor antagonists, which were initially developed as antihypertensive agents. Tamsulosin hydrochloride is clinically important drug as far as benign prostatic hyperplasia is concerned. Thus in this review all of the analytical methods reported in the literature are summarized. Different spectrophotometric, chromatographic, electroanalytical and some other types of analytical methods were discussed here. Analytical methods were compared in terms of sensitivity, range, applications and economy. The presented review is helpful for the researchers involved in the development of new analytical methods or formulations of Tamsulosin hydrochloride.

Keywords: *tamsulosin hydrochoride, spectrophotometry, chromatography, analytical methods for tamsulosin hydrochloride, electroanalytical method for tamsulosin hydrochloride*

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1. Introduction

Management of lower urinary tract symptoms (LUTS) and benign prostatic hyperplasia (BPH) has been central to urology for decades. The urologic community has increasingly come to realize that many men with LUTS do not have prostate enlargement and do not need their prostates debulked surgically [1].

Benign prostatic hyperplasia (BPH), a urological disorder which is highly prevalent in the aging male population affecting over 50% of men above the age of 60, leads to a variety of symptoms including increased frequency of urination, poor stream of urine flow, dribbling, nocturia, hesitancy in starting urine flow, and large residual volumes [2]. In benign prostatic hyperplasia (BPH) there will be a sudden impact on overall quality of life of patient. This disease occurs normally at the age of 40 or above and also is associated with sexual dysfunction [3].

The goal for BPH should be to relieve bothersome symptoms and to reduce the risk of progression to potentially serious outcomes such as acute urinary retention (AUR) and BPH-related surgery [4]. According to the EAU 2011 guidelines, alpha-blockers are currently the preferred first-line therapy for all men with moderate or severe LUTS/BPH. The amount of prescriptions for α-blockers has been increasing steadily in the last 10 years [5]. The α_1-blockers relieve the smooth muscle tension within the prostate and bladder neck approximately two weeks after their administration [6].

α_1-Adrenergic receptors are subdivided into α_{1A}, α_{1B}, and α_{1D} subtypes, and antagonists include quinazoline based prazosin, doxazosin (dox), and terazosin and the sulfonamide derivative tamsulosin [7]. Among the currently available alpha-blockers, tamsulosin is selective to the alpha$_{1A}$-adrenergic receptor subtype that is predominant in the human prostate, whereas other alpha-blockers do not discriminate among alpha-adrenergic receptor subtypes [8,9].

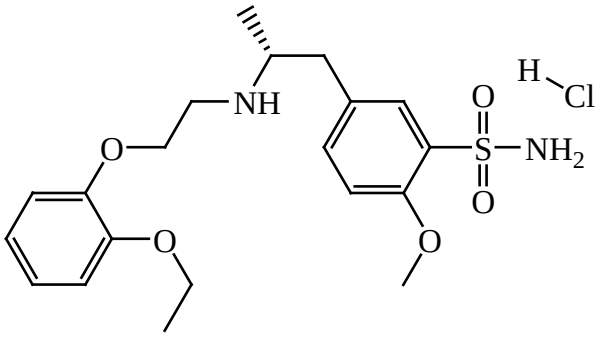

Figure 1. Chemical structure of Tamsulosin hydrochloride

Tamsulosin hydrochloride is the international non-proprietary name of (-)-(*R*)-5-[2-[[2-(o-ethoxyphenoxy) ethyl]amino]propyl]-2-methoxybenzenesulfonamide hydrochloride (Figure 1), was first developed by Yamanouchi Pharmaceuticals and is currently marketed as a single enantiomer [10]. Tamsulosin is a chiral molecule and its (*R*) enantiomer is used as a therapeutic active substance [11].

It has a better side effect profile than earlier α-adrenergic-receptor antagonists, which were initially developed as antihypertensive agents. Clinical trials of 1 year or longer with tamsulosin showed high tolerability for the 0.4mg dose and no significant interaction with other antihypertensive medications. Tamsulosin is a more selective α_{1A} subtype antagonist, which maintains the α-antagonist effect on the prostatic capsule and bladder neck but has less of an effect on the vascular system and blood pressure. In fact, tamsulosin is ineffective and not indicated in the treatment of hypertension. Tamsulosin has a favorable side effect profile in regard to problems related to hypotension and dizziness compared to those of terazosin and doxazosin [12].

Combining α_1-ARAs and antimuscarinic agents [e.g Tolterodine Tartarate] in the treatment of BPH resulted in statistically significant benefits in QoL scores, patient satisfaction, urinary frequency, storage symptoms and IPSS scores. The combination of α1-ARAs with antimuscarinic agents is useful for relieving symptoms of bladder outlet obstruction (BOO) and detrusor overactivity (DO). Also the combination of α1-ARAs and 5 α-reductase inhibitors [e.g. Dutesteride and Finasteride] appears to prevent disease progression in patients [13].

Tamsulosin is absorbed from the gastro–intestinal tract; 90% following oral administration. The extent and rate of absorption is reduced in the presence of food. It is distributed into extracellular fluid in the body. The drug is metabolised slowly in the liver by hepatic metabolism while first-pass metabolism is negligible. It is mainly metabolised by the cytochrome P_{450} CYP3A enzyme and less than 10% of the dose is excreted in urine unchanged. The metabolites of tamsulosin hydrochloride undergo extensive conjugation to glucuronide or sulfate prior to renal excretion. It is excreted mainly in urine as metabolites and some unchanged drug. The apparent half–life is approximately 9 to 13 h in healthy individuals and 14 to 15 h in the target population [14].

Thus there is no doubt that tamsulosin is clinically important alpha one blocker. This forms the background of our study. There is clear need to study all of the analytical methods available in different matrices. Different analytical methods such as spectrophotometry, chromatography and electroanalytical methods will be discussed here. The presented study provides substantial information to the researchers involved in the development of new analytical methods and formulation development.

Review of analytical methods for the determination of five alpha one blockers was published by Shrivastava et al [15]. In this review authors also described tamsulosin determination methods available during the preparation of manuscript. In this paper authors focused in the determination methods of tamsulosin because of its proved clinical advantages over other alpha one blockers. This review differs in advancement of technology by inclusion of 30 more references of analytical methods for Tamsulosin.

In search for analytical methods for the determination of tamsulosin hydrochloride database like Sciencedirect, Pubmed, Medknow, NCBI, Taylor and Francis and Google scholar were explored by using keywords "Analytical methods for tamsulosin", "Determination of tamsulosin", "Spectrophotometric method for tamsulosin determination, "Chromatographic method for tamsulosin determination", "Electroanalytical methods for determination of tamsulosin". Total 82 different analytical methods were found including 24 spectrophotometry, 46 chromatography, 11 electroanalytical (including pharmacopoeia references) and 1 redioreceptor methods for the determination of tamsulosin hydrochloride either alone or in combination in different matrices.

2. Analytical Methods

Tamsulosin hydrochloride 5-[(2R)-2[[2-(2-Ethoxyphenoxy) ethyl]amino]propyl]-2-methoxybenzenesulfonamide hydrochloride is white or almost white powder slightly soluble in water, freely soluble in formic acid, slightly soluble in anhydrous ethanol. [16] Drug is official in JP [17], Eu Ph [16], USP [18] and BP [19].

Analytical methods for the determination of TAM are divided into three main categories, spectrophotometry, chromatography and other electroanalytical methods. Summary of all of the spectrophotometric methods are given under Table 1 and Table 2. Chromatographic methods are summarized under Table 3 and Table 4 whereas in Table 5 all electroanalytical methods for TAM determination are presented.

2.1. Spectrophotometric Methods

During the 1980s, the introduction of miniature diode array detectors, combined with powerful microprocessors and state-of-the-art mathematical tools, led to a renaissance of ultraviolet visible (UV/vis) spectrometry that enabled the rapid spread of compact, relatively low-cost, yet still powerful, laboratory UV/vis machines [20]. One of the interesting aspects of UV spectrophotometry is its low cost and its ease of use, allowing many measurements in a short time [21]. Derivative spectrophotometry, which consists in the differentiation of a normal spectrum, offers a useful means for improving the resolution of mixtures, because it enhances the detectability of minor spectral features [22].

Total 25 different spectrophotometric methods for the determination of TAM in either bulk or formulations are available. There is no doubt on the fact that the spectroscopic methods are rapid and far more economical than chromatographic methods, but their destructive nature and lack of sensitivity is a huge disadvantage [23,24]. Morever, TAM has high potency (0.4mg/tab/cap) and may be this is one of the reason that spectrophotometric method or determination in biological matrices is not available. Analytical methods for the determination of tamsulosin alone is presented in Table 1 whereas Table 2 presents literatures related to combinations with other drugs.

Table 1. Summary of spectrophotometric methods for determination of Tamsulosin

Principle	Wavelength	Linear range	LOD	LOQ	Application	Ref
Simple dilution in Methanol	281nm	5-25µg/ml	NM	NM	Capsules	[25]
First Order Derivative Spectroscopy	234.5nm	5-25µg/ml	NM	NM		
AUC Method	286.0-276.0nm	5-25µg/ml	NM	NM		
Simple dissolution in distilled water	279nm	1-6µg/ml	NM	NM	Tablets	[26]
First Order Derivative Spectroscopy	298nm	1-6µg/ml	NM	NM		
AUC Method	263-298nm	1-6µg/ml	NM	NM		
Zero order	280nm	10-90µg/ml	NM	NM	bulk drug and tablet	[27]
First order	298nm	10-90µg/ml	NM	NM		
Reaction between drug and bromophenol blue	421nm	2.5-22.5µg/ml	0.003µg/ml	0.01µg/ml	tablet and capsule	[28]
Bromination with a known excess amount of Bromate-bromide mixture in acidic medium followed by the determination of surplus bromine by reacting with dye methyl orange	513nm	2-12µg/ml	0.57µg/ml	1.74µg/ml	tablets	[29]
Spectrofluorimetric	λ_{ex} 226 nm λ_{em} 322nm	5-30µg/ml	1.36µg/ml	4.92µg/ml	tablet	[30]
3 ml 400 µg/ml [in 0.1M NaOH] 1.0ml of folin reagent (1.092×10^{-2} M), 5.0ml of buffer pH 8.0 and 1.5ml of distilled water were added and kept aside for 15 min. Volume was made up to 25ml using distilled water and sonicated for 1 min. [Final dilution 48µg/ml]	440nm	16-48µg/ml	NM	NM	Tablets and capsules	[31]
The 3.0ml of 200µg/ml [in 0.1 M NaOH] was taken in 25ml calibrated tubes containing 15 ml of buffer pH 8.0. 1.0ml each of Sodium nitroprusside solution and acetaldehyde were added successively and shaken for 2 minutes and kept aside for 15 minutes at room temperature and made up to the mark with distilled water and sonicated for 1 min [Final dilution 24µg/ml]	560nm	8.0-24µg/ml	NM	NM		
Reaction with 0.3% 4-aminoantipyrine (0.5mL) and 0.5% ammonia (2.0mL)	400nm	4-20µg/ml	NM	NM	Bulk and capsules	[32]
Reaction with 0.5% orcinol (0.5mL) and 0.5 % ammonia (2.0mL)	440nm	4-20µg/ml	NM	NM		
Reaction with 0.5% resorcinol (0.5mL) and 0.5% ammonia (1.0mL)	430nm	4-20µg/ml	NM	NM		
Reaction with 2.0mL of 0.1% eriochrome black T	520nm	4-20µg/ml	NM	NM		

NM: Not mentioned

Table 2. Summary of spectrophotometric methods of Tamsulosin HCl in combination with other drugs

Drugs	Principle	Wavelength	Linear range	LOD	LOQ	Application	Ref
Tamsulosin+ Finasteride	Simple simultaneous determination	224nm	1-5µg/ml	NM	NM	Bulk and formulations	[33]
	Ratio derivative spectroscopy	229.91nm	2-10µg/ml	0.19µg/ml	0.54µg/ml	Tablets	[34]
Tamsulosin+ Tolterodine	Areas under the curve	230.5-220.5nm	5-25µg/ml	NM	NM	Capsules	[35]
	First order derivative spectroscopy	221.5nm	5-25µg/ml	NM	NM		
Tamsulosin+ Dutasteride	Ratio Derivative	234.20nm	4-20µg/ml	NM	NM	Capsules and tablets	[36]
	Dual wavelength Method	272.35 nm and 276.05nm	4-20µg/ml	NM	NM		
Tamsulosin+ Finasteride	Simple simultaneous equation method	225nm	1-10µg/ml	0.3µg/ml	1µg/ml	Capsules	[37]
Tamsulosin+ Dutasteride	First order derivative	232.60nm	8-40	NM	NM	Capsule and Tablets	[38]
	Areas under the curve	222.50-223.62nm	4-20	NM	NM		
Tamsulosin+ Alfuzosin, Terazosin, Doxazosin, Prazosin	Negative result						[39]

NM: Not mentioned

Table 3. Summary of chromatographic procedures found in literature survey for the determination of Tamsulosin HCl in different matrices

Method	Chromatographic condition	Linear range	LOD	LOQ	Application	Reference
LC-MS/MS	Bonchrom XBP-C_{18} column using a mobile phase consisted of methanol-acetonitrile-ammonium formate (10mmol x L^{-1}) (30 : 40 :30, v/v/v), at a flow rate of 0.4 mL x min^{-1}	0.02 - 50ng/ml	NM	0.02 ng/ml	In dog plasma after oral administration of controlled-release tablet	[44]
LC–MS–MS	J'sphere ODS-80H column (75mm×34.6mm I.D., 5µm, YMC, Tokyo, Japan). Mobile phase: 50mM acetic acid adjusted to pH 4.0 with 50mM ammonium acetate and methanol (4:6 v/v). Column temperature: 40°C. Flow-rate: 0.5ml/min	10–1000pg/ml in plasma dialysate, 0.5–50ng/ml in plasma, and 1–100ng/ml in urine	NM	NM	In human plasma dialysate, plasma and urine	[45]
LC–ESI-MS	C_{18} reversed-phase column using a mobile phase of methanol–water–acetic acid–triethylamine (620:380:1.5:1.5, v/v).	0.2–30ng/ml	NM	0.1ng/ml	Pharmacokinetics in adult humans	[46]
HPLC-UV	Chiralcel OD-RH column (250mm × 4.6mm, Daicel Chemical Industaies.Ltd, Japan) packed with 5µm silica gel coated by Cellulose tris(3,5-dimethylphenylcarbamate)with a binary solvent mixture of 50 mmol l^{-1} KPF_6–acetonitrile (v/v (70:30), pH 5.0). Flow rate: 1 ml/min. Wavelength 225 nm. Column temperature 25-30°C.	0.03–6.0 µgml^{-1} for *R*-isomer and 0.028–5.6 µgml^{-1} for *S*-isomer	0.11 for both *R* & *S* resp	0.44ng for both *R* & *S* resp	Separation of tamsulosin and its *S*-isomer	[47]
HPLC-F	Octadecylsilica column (55mm × 4mm, 3µm particles). Mobile phase: acetonitrile–30mM dihydrogenpotassium phosphate (25:75 v/v). 228/326nm (excitation/emission wavelength).	0.397–40.50ng/ml	NM	0.4ng/ml using 1ml of plasma	In human plasma	[48]
LC-TMS	Zorbax Extend-C_{18} column (150mm × 4.6mm i.d., 5µm, Agilent, Palo Alto, CA, USA) with a SecurityGuard C_{18} guard column (4mm×3.0mm i.d., Phenomenex, Torrance, CA, USA). Mobile phase: Methanol, water and formic acid (80:20:1, v/v/v) was delivered at a flow rate of 0.5ml/min. Column temperature 20°C.	0.1–50.0ng/ml	-	0.1ng/ml	Dog plasma	[49]
LC–MS/MS	Waters XTerra C_8 column (50mm×2.1mm, 3.5µm, Waters, Milford, MA, USA) and a Zorbax XDB-C_8 Narrow-Bore Guard Column (Agilent Technologies, Palo Alto, CA, USA). The mobile phase consisted of water–formic acid (A; 100:0.1, v/v) and water–acetonitrile–formic acid (B; 50:50:0.1, v/v/v). The gradient programwas as follows: 0–5min: 10% B→100% B; 5–6 min: 100% B→10% B; 6–8 min: 10% B→10% B. Column temperature 30°C.	0.1–4.7ng/ml and 0.1–19.3ng/ml for aqueous humor and serum samples resp.	NM	0.1 ng/ml for both human aqueous humor and serum samples	Human aqueous humor and serum	[50]
RP-LC/ESI-MS–MS*	Hypersil BDS C_{18} (250mm×4.6 mm) 5µm (Thermo Electron Corporation, Runcorn, UK). Inertsil ODS 3v (250mm×4.6mm) 5µm (G.L. Sciences, Tokyo, Japan). XTerra C_{18} (250mm×4.6mm) 5µm (Waters, Milford, MA, USA). Kromasil KR100-5C_{18} (250mm×4.6mm) 5µm (Eka Chemicals, Bohus, Sweden). Symmetry C_{18} (250mm×4.6mm) 5µm (Waters, Milford, MA, USA). Mobile phase was 10mM ammonium acetate– acetonitrile in a gradient elution mode of a flow rate of 1.0ml/min at 30°C. Photodiode array detector 280nm	0.5 to 5.0µg/ml	0.06–0.11µg/ml	0.21-0.39 µg/ml	Bulk drugs and formulations	[51]
HPLC-UV	Lichrosphere ODS C_8 RP Column (4.6mm ID, 250mm L, particle size 5 Micron, at wavelength of 280nm. Mobile phase (Potassium Dihydrogen Orthophosphate and Acetonitrile) at the flow rate of 1.2ml/min. λ = 280nm	NM	NM	NM	Analysis in bulk drugs	[52]
HPTLC	Aluminium plates pre-coated with silica gel 60F_{254} as the stationary phase and the mobile phase consisted of acetonitrile/methanol/dichloromethane (2.0: 1.0: 2.0, v/v/v)	300–800ng	8.49ng per	25.72ng per band	Tablets	[53]

HPLC-UV	Inertsil ODS 3V (5 µ, 15 x 4.6mm) column, in an isocratic mode, using acetonitrile:buffer (30 : 70) as mobile phase. pH 3 adjusted with perchloric acid. Flow rate 2 mL/minute and elution monitored at 220 nm.	100 to 500µg/ml	NM	NM	Pellets 0.2%	[54]
HPLC-UV	ODS, Phenomonex,C_{18} (250x4.6 mm, 5µ) column using a mobile phase consisting of sodium dihydrogen orthophosphate buffer-Acetonitrile (70:30).The eluent was monitored at 280nm.	NM	NM	NM	bulk and tablet	[55]
HPTLC	Aluminium plates pre-coated with silica gel 60F-254 as stationary phase. The solvent system consisted of toluene-methanol-triethylamine 9:3:1 (v/v/v).	200–3000ng	10ng	50ng	bulk and tablets	[56]
HPLC-UV	C_{18} column using gradient LC method, solution A: aqueous ortho phosphate buffer pH 6.5 and B: mixture of water: acetronitrile (90:10%v/v). The method was linear over a range of 0.2 to 1.9µg/ml. λ = 286nm	0.2 to 1.9µg/ml	0.007µg/ml	0.020µg/ml	intermediates in the reaction mixtures and the finished products	[57]
HPLC-UV	Supelcosil LC-18 column (25cm×4.6mm; 5 mm particle size) preceded by a Sentry guard column. Mobile phase: acetonitrile 70% (pH 3.4 adjusted with glacial acetic acid), flow rate of 0.75mL/min. Photodiode array detector at 225nm.	0.025–1.00mcg/mL.	0.015µg/ml	0.025µg/ml	dissolution study of OMNIC® capsules	[58]
HPTLC	Aluminium plates precoated with silica gel $60_{F\text{-}254}$ as the stationary phase while the solvent system consisted of toluene : methanol : triethylamine (3.5 : 1.2 : 0.2v/v). Absorbance mode at 280 nm.	400–2400 ng per spot	20.49 ng per spot	62.10 ng per spot	Bulk and tablets	[59]
HPLC-UV	ODS C_{18} Column 250 X 4.6 mm (particle size of 5µ), Mobile phase: acetonitrile: (0.05M) KH_2PO_4 buffer (45:55) at flow rate 1.8ml/min, monitored at 240nm.	10-50µg/ml	0.495µg/ml	0.461µg/ml	Bulk and tablets	[60]
HPLC-UV	Microbondapak C18 (Lichrospher, Darmstadt, Germany) column of 250mm × 4.6mm i.d. particle size of 5µm. C_{18} column with a simple isocratic mobile phase consisting methanol: 50mM phosphate buffer (pH 7.8, ratio 80:20) at a flow rate of 1 ml/m. λ = 230nm	5-250µg/ml	10ng/ml	50ng/ml	tablets	[61]
HPLC-UV	Chiral separations were performed using 4.6×250mm,5µm, columns: Chiralcel OD-H (cellulosetris (3,5-dimethylphenylcarbamate)) and Chiral pakAD-H (amylosetris (3,5-dimethylphenyl carbamate)) from Daicel Chemical Industries Ltd. Mobile phase: hexane–isopropylalcohol– triethylamine (80:20:0.2, v/v/v), flowrate 1.2 ml/min, detection UV 279nm, *t* = 25°C.	1–100µg/ml	0.2µg/ml [both isomers]	0.6µg/ml [both isomers]	Enantioseparation & determination of(*R*,*S*)-isomers in tablet and capsules formulations	[62]
LC–MS/MS	Luna C_{18} column (2.0mm × 50mm, 5µm particles) with a mobile phase of 10 mM ammonium formate buffer (pH 3.5)–methanol (25:75, v/v) and quantified by MS/MS detection in ESI positive ion mode. The flow rate of the mobile phase was 200 µL/min. *t* = 30°C	0.01–20ng/mL	0.01ng/mL	-	Pharmacokinetic study in humans.	[63]
HPLC-UV	Lichrocart / Lichrosphere C_{18} column (250 x 4.0mm packed with 5 µ) with mobile phase consisting of a mixture of Acetonitrile: T.D.W. in the ratio (40: 60). Flow rate was 0.8 mL / min. Detection at 275nm.	1-200µg/mL	0.36µg/mL	0.74µg/mL	tablets	[64]
HPLC-UV	Inertsil ODS 3V (5 microns,15cm x 4.6mm).Mixture of 100 ml Perchloric acid solution + 565ml water. Adjust pH=2.0 with 1N sodium hydroxide solution or with perchloric acid solution. Diluted with water to 700ml and added 300ml acetonitrile. λ = 220nm.	100-500µg/ml.	NM	NM	pellets	[65]
HPLC-UV	C_{18} column with a mobile phase consisting of acetonitrile and water in the ratio of 50:50 v/v. The mobile phase was pumped at a flow rate of 1.5ml/min. The eluents were monitored at 214nm	5 to 100µg/ml	0.019µg/ml	0.0575µg/ml	tablets	[66]

LC-MS	Nucleosil C_{18}, 5 µm (125 mm x 4.0 mm i.d.) column with oven temperature at 40°C. Mobile phase consisted of methanol and 0.05M ammonium acetate buffer pH 3.7 (6:4, v/v, flow rate v/v, flow rate at 0.5mL/min)	0.7-35ng/ml	0.1ng/mL	0.7ng/mL	bioavailability studies	[67]
HPLC-UV	Dissolve 3.0g of sodium hydroxide in a mixture of 8.7mL of perchloric acid and 1.9L of water; adjust to pH 2.0 with 0.5M sodium hydroxide and dilute to 2L with water; to 1.4L of this solution, add 600mL of acetonitrile. ODS column, (150×4.6mm), 5µ particle size. t = 40°C. Flow rate 1.3ml/min, λ = 225nm.	NM	NM	NM	Related substances	[19]
HPLC-UV	Column 250×4.6mm, Silica gel for chiral separation, Mobile phase diethylamine, methanol, anhydrous ethanol, hexane (1:150:200:650 V/V/V/V). Flow rate 0.5mL/min. Detection Spectrophotometer at 225nm. t = 40°C.	NM	NM	NM	Enantiomeric purity	
HPLC-UV	A stainless steel column 4 mm in inside diameter and 15cm in length, packed with octadecylsilanized silica gel for liquid chromatography (5mm in particle diameter). t = 40°C. Mobile phase: Dissolve 4.4mL of perchloric acid and 1.5g of sodium hydroxide in 950mL of water, adjust the pH to 2.0 with sodium hydroxide, and add water to make 1000 mL. To 700mL of this solution add 300mL of acetonitrile. Adjust the flow rate so that the retention time of tamsulosin is about 6 minutes. (wavelength: 225nm)	NM	NM	NM	Related substances	[17]
LC-MS	Nucleosil C_{18}, 5µm (125mm x 4.0mm i.d., Phenomenex, USA) column with oven temperature of 40°C. The mobile phase consisted of methanol and 0.05M ammonium acetate buffer pH 3.7 (6 : 4, v/v) and the flow rate was 0.5µL/min.	0.7-35.0 ng/ml	0.1 ng/mL	0.7ng/mL	Pharmacokinetics study	[68]
HPLC-UV	Inertsil ODS 3V, 150mm × 4.6mm × 5µm or its equivalent in isocratic mode, with mobile phase compressing of Buffer: Acetonitrile(70:30) The flow rate was 1.5ml/min and the detection was carried out by PDA detector i.e., 225nm	80 to 120µg/mL	0.1920 µg/mL	0.5813µg/mL	Pellets	[69]
HPLC-UV	Ace 5-C_{18} (250×4.6mm, 5µm) column, and 10 mmol L^{-1} methanol and water (70:30 v/v) as a mobile phase. The detection was at the wavelength of 280 nm. Flow rate 1ml/min.	2-30µg/ml	0.24 µg/ml	0.73µg/ml	Bulk and tablets	[70]
LC-MS	Waters symmetry C_{18} column with a mobile phase of 0.03% formic acid–acetonitrile (30:70, v/v)	0.1–50.0ng	NM	100pg/ml	Pharmacokinetic, bioavailability or bioequivalence studies	[71]
HPLC-UV	ODS (150mm×4.6mm,5µm ）Column, using methanol-0.2mmol·L-1 Na2HPO4-KH2PO4 （pH 5.9 ） （6:4 ） as the mobile phase. The flow rate was 1.0mL·min-1,the detection was set at 275nm and the column temperature was maintained at 30°C.	NM	NM	NM	Yankening and Yujin Yinxie tablets.	[72]
HPLC-UV	ODS (150mm ×4.6mm,5µm) column,using methanol-0.2 mmol/L^{-1} Na_2HPO_4-KH_2PO_4 (pH 5.9)(6:4) as the mobile phase. The flow rate was 1.0mL/min^{-1}, the detection wavelength was set at 275nm and the column temperature was 30°C.	5.06-130.65µg/mL	NM	NM	Capsules and related substances	[73]
UPLC–MS–MS	Acquity UPLC Beh C_{18}, 2.1 × 50mm, 1.7 µm, Mobile phases: A: 0.1% HCOOH in water B: MeOH, Gradient: 95% A to 25% A in 1 min, hold 0.5 min, ramp to 2% A in 0.1 min and hold for 0.4 min return to initial (2.5 min total cycle time), Flow-rate: 0.6 mL/min, Temperature: 35°C	0.01 to 10ng/mL.	NM	0.01ng/mL	Tamsulosin (Flomax) in Human Plasma	[74]

HPLC-UV	Chiralcel OD-R column (250×4.6, 10µ). Mobile phase: mixture of 0.5mol/L sodium perchlorate and acetonitrile (80:20, *v/v*, pH 4.0). Flow rate 0.4 ml/min, detection 223nm.	NM	NM	NM	Enantiomers and synthetic intermediates of drug	[75]
HPLC-UV	Chiralpak AD-H column (250 ×4.6mm, 5µ, Daicel make). Mobile phase: hexane:isopropanol:methanol (65:15:25, *v/v/v*). Wavelength: 225nm	0.5-3.0mg/ml	150ng/ml	50ng/ml	Enantiomers separation	[76]
HPLC-UV	Zorbax SB-CN 250×4.6mm, 5µ column. Mobile phase: 10 mM ammonium acetate-ACN (40:60, *v/v*). wavelength 225nm. Flow rate 1 ml/min	25-150µg/mL	NM	NM	Separation of impurities and drug	[77]

NM: Not mentioned

Table 4. Summary of chromatographic methods for the determination of tamsulosin HCl in combination with other drugs

Drugs	Methods	Chromatographic condition	Linear range	LOD	LOQ	Application	References
Tamsulosin and Dutasteride	LC–MS–MS	Gemini C-18, 50mm × 2.0mm (3µm) column and using methanol:ammonium formate (97:3, v/v)	2-25ng/ml	NM	1ng/ml	Human Plasma	[78]
Tamsulosin and finasteride	HPLC-UV	Phenomenex C_{18} column using methanol/0.02 mol L^{-1} ammonium acetate buffer /triethylamine (79.9 + 20 + 0.1, *v/v/v*) (pH 9.2) as mobile phase. λ = 235nm	0.5–16µg/ml	0.2µg/ml	0.5µg/ml	Bulk and tablets	[79]
	TLC	silica gel 60 F_{254} using toluene/ methanol/ triethylamine (9 + 1.5 + 1, *v/v/v*), λ = 270 nm,	100-2000ng per spot	80ng per spot	100ng per spot	Bulk and tablets	
	HPLC-UV	Shimadzu HPLC, 10-At detector with hypersil ODS C_{18} Column 250 ×4.6mm (particle size of 5µ) and constant flow pump. Mobile phase: acetonitrile: (0.05M) KH2PO4 buffer (45:55) at flow rate 1.8ml /min. The detection was monitored at 240nm.	25-625µg/ml	0.495µg/ml	1.635µg/ml	Bulk and tablets	[80]
	HPTLC	Aluminum plate precoated with silica gel 60 F254 using toluene: n-propanol: triethylamine 3.0:1.5:0.2 v/v) as mobile phase. Detection was carried out densitometrically at 260nm.	200-1200ng/spot	17.47ng	52.94ng	tablet	[81]
	HPLC-UV	C_{18} column (150 x 4.6 mm, 5 µ) with a mobile phase consisting of a mixture of methanol and formic acid (0.02% v/v in water) at a flow rate of 1 mL/min and ran in gradient mode. Detection was carried out at 230nm.	0.4-20µg/mL	0.16µg/mL	0.49µg/mL	tablet	[82]
	HPLC-UV	RP C_{18} BDS column (250mm×4.6mm, 5µm) with a mobile phase consisting of methanol: water (70:30, v/v) (pH 3.7) adjusted with ortho phosphoric acid, with a flow rate of 1ml/min, UV detection at 260nm was used.	4-24 µg/ml	1.03µg/ml	0.28µg/ml	tablets	[83]
	HPLC-UV	C_{18}, (250×4.6mm, 5µm). Mobile phase ACN:water, 60:40. Wavelength 240nm	0.2-0.8µg/ml	NM	NM	Capsules	[84]
Tamsulosin, Prazosin, Terazosin, Doxazosin and Alfuzosin	HPLC-UV	Kromasil C_{18} column (250 × 4.6mm, 5.0 µm) from Agilent Technologies, a UV detector at 230nm and a elution was performed under a gradient mobile phase composed of (A) ACNdiethylamine (0.05mL), (B) methanol, (C) 10mM ammonium acetate and (D) Water.	2-8µg/ml	0.11µg/ml	0.363µg/ml	Bulk and formulations	[85]

2.1.1. Comparison of Spectrophotometric Methods

Tamsulosin HCl is a potent drug [0.4/mg/cap/tab] and this is the reason there are attempts to enhance UV absorbance by addition of chromophore by some of the authors. [28,29,30,31,32]. Although UV spectrophotometric methods have advantage of simplicity and economy over chromatographic methods but it's difficult to develop highly sensitive determinations in biological fluids. In this case there sensitivity is questionable. This may be the reason that no author till date attempted spectrophotometry method for complex matrices like biological fluids. High potency of the drug further enhances the difficulty to develop such kind of methods. However method using water for preparing dilution [26] seems to be most economical and simple method. Derivative spectrophotometry may be better option for resolving mixtures in simultaneous determinations. With LOD and LOQ of 0.003µg/ml 0.01µg/ml method developed by Shrivastava et al. [28]. is the most sensitive method available in the literature.

2.2. Chromatographic Methods

Analytical chemists have to analyze a variety of complex samples often originating in different matrices to

answer questions about the quality and quantity of different analytes. These requirements are satisfied with HPLC especially if combined with an advanced detection technique such as diode array detection (DAD) or mass spectroscopy [40].

HPTLC allows fast and inexpensive method of analysis in the laboratory and in the field. The modern HPTLC technique, combined with automated sample application and densitometric scanning, is sensitive and completely reliable, suitable for use in qualitative and quantitative analysis. HPTLC is a valuable tool for reliable identification because it can provide chromatographic fingerprints that can be visualized and stored as electronic images [41,42]. HPTLC remains one step ahead when compared with other tools of chromatography [43].

Summary of all of the chromatographic methods found in the literature survey for Tamsulosin alone and in combinations are presented under Table 3 and Table 4 respectively.

Table 5. Summary of electroanalytical methods found in literature survey

Method	Principle	Linear range	LOD	LOQ	Application	References
Voltammetry	Cyclic, linear sweep, differential pulse (DPV) and square wave voltammetry (SWV)	2×10^{-6} and 4×10^{-4} M for DPV & SWV resp	3.34×10^{-7} M for DPV and 2.45×10^{-7} M for SWV	1.11×10^{-6} 8.16×10^{-7} M for DPV & SWV resp	Capsules and in vitro determination of TAM in spiked serum samples	[87]
Capillary electrophoresis	Uncoated fused silica capillary (CACO-Sila Tubing and Optical Fibbers, Slovakia) of the total and effective lengths of 33 and 24.5cm, respectively, and 50µm i.d.×365µm o.d., diode array detector at 200nm. Capillary was thermostated at 25°C, the applied voltage was 20kV (606Vcm^{-1}). Background electrolytes: dissolution of acetic acid in deionised water (18MΩcm^{-1}; Elga, Bucks, England) and pH was adjusted with sodium hydroxide.	6×10^{-6} to 6×10^{-5} mol l^{-1}.	1.6×10^{-6} mol l^{-1} for *R*-isomer and 1.7×10^{-6} mol l^{-1} for *S*-isomer	5.3×10^{-6} mol l^{-1} for *R*-isomer and 5.7×10^{-6} mol l^{-1} for *S*-isomer	Determination of both enantiomers and applied for quality control and fast screening metabolic studies	[88]
Capillary electrophoresis	Cyclodextrin (CD)-mediated capillary electrophoresis (CE) with DAD at 200nm. 20kV with 30cm × 50µm I.D. polyacrylamide (PAA)-coated fused-silica capillary (effective length 20cm) and running buffer with sulfated- β -CD (S-β-CD) as chiral selector. The running buffer was prepared by dissolving S-β-CD in an appropriate volume of phosphoric acid (100 mmol l^{-1}). pH adjusted to 2.5 by using TRIS*.	50.0–500.0 µmol l^{-1} for both isomers	20 and 40 µmol l^{-1} for *R*- and *S*-isomers resp	80 and 120 µmol l^{-1} for *R*- and *S*- isomers resp	Capsule formulations	[89]
Capillary electrophoresis	An uncoated fused silica capillary of 50mm I.D. and 33cm (24.5cm effective length). 100 mM tris (hydroxymethyl) aminomethane buffered with phosphoric acid to pH to 2.5, concentration of sulfated-β-cyclodextrin, 0.15% (W/V), column temperature 25°C, and applied voltage of 25kV.	NM	NM	NM	Separation of enatiomers	[90]
Capillary electrophoresis	Sulfated β-cyclodextrin was used as a chiral selector. In acidic electrolytes, sulfated b-cyclodextrin migrates as an anion and the analyte (tamsulosin) migrates as a cation. Electrolytes were prepared by dissolving an appropriate amount of acetic acid in water, adjusted to pH 4.0 with sodium hydroxide or Tris. Detection wavelength 210nm.	NM	NM	NM	Separation of enantiomers	[91]
Conductometric method	4.45-44.50mg TAM were titrated 10^{-2} against Phospho tungestic acid (PTA) $H_3[PW_{12}O_{40}.xH_2O]$, silicotungestic acid (STA) $H_4[SiW_{12}O_{40}]$, or sodium tetraphenyl borate (NaTPB) $Na[C_{24}H_{20}B]$	-	-	-	Capsules	[92]
Voltammetric sensor	Multiwalled carbon nanotubes (MWNTs)–Nafion-modified glassy carbon electrode (GCE). At MWNT-modified electrode, TAM gave a well-defined oxidation peak at a potential of 1084mV in 0.1M acetate buffer solution of pH 5.	1×10^{-3} M–3×10^{-7} M	9.8×10^{-8} M	NM	Formulations and urine samples	[93]

NM: Not mentioned

2.2.1. Comparison of Chromatographic Methods

Overall 45 different chromatographic methods reported in the currently available literature for the determination of Tamsulosin either alone or in combinations with other drugs. Out of this 28 HPLC-UV, one UPLC-MS-MS, one TLC, three HPTLC, and rest of the methods reported with mass spectrometer as detector equipped with liquid chromatography. HPLC-UV methods are economical methods but are less sensitive in comparison to HPLC-MS.

Most sensitive chromatographic method reported is UPLC-MS-MS method [LOQ 0.10ng/ml]. Although with LOQ of 0.4ng/ml HPLC-F method is also one of the most sensitive method on records for tamsulosin determination. With LOQ of 0.02µg/ml Sudha and Dhomane [57] is most sensitive method among HPLC-UV method. However LOD and LOQ value also depends upon the noise of the detector and the matrix. *S*-isomer of the drug is available in the form of impurity and of not much therapeutic interest thus methods for separation of enantiomers [47,62,19,75,76,77] are also appreciable.

2.3. Electroanalytical Methods

Modern electrochemical methods are now sensitive, selective, rapid, and easy techniques applicable to analysis in the pharmaceutical fields, and indeed in most areas of analytical chemistry. They are probably the most versatile of all trace pharmaceutically active compound analysis [24]. Electroanalytical techniques can easily be adopted to solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity and selectivity, often in a spectacularly reproducible way by employing this approach [86].

All of the electroanalytical methods found in literature available related to determination of tamsulosin HCl is presented under Table 5.

2.3.1. Conductometric

The conductometry is the analytical method used both in research laboratories as well as in industry [94]. Conductometry provide convenient mean for the determination of end point in the titration [95]. Since tamsulosin hydrochloride is able to form precipitates with heteropoly acids, phosphotungestic, silicotungestic, and sodium tetraphenylborate so the applicability of conductimetric titration of these drugs with the above mentioned reagents, was tested by Abdel-Moety et al. [92]. There was no effect in the shape of titration curve upto 50°C and titrant solutions lower than 10^{-2}M are not suitable for conductimetric titrations because of unstable readings.

2.3.2. Voltammetric

Voltammetry encompasses a group of electrochemical technique in which potential is applied to an electrochemical cell with the simultaneous measurement of the resulting current. By varying potential in the electrodes, it is possible to oxidize or reduce analytes in the solution [96]. the method developed by Ozkan *et al*. [87] is one of the most sensitive analytical method reported for tamsulosin determination. Authors claim that procedures did not require sample pre-treatment or any time-consuming extraction step prior to drug assay. Another method developed by Lonappan *et al*. [93] using differential pulse voltammetric sensor for the determination of tamsulosin hydrochloride (TAM) using multiwalled carbon nanotubes (MWNTs)–Nafion-modified glassy carbon electrode (GCE).

2.3.3. Potentiometric

Potentiometry is a classical analytical technique with roots before the twentieth century. However, the rapid development of new selective electrodes and more sensitive and stable electronic components since 1970 has tremendously expanded the range of analytical applications of potentiometric measurements [97]. May be this is one of the reason that potentiometric measurements are official methods in all pharmacopeias [16,17,18,19] for determination of Tamsulosin HCl. In thses methods 0.1 N perchloric acid is used as titrant and end point was determined potentiometrically.

2.3.4. Capillary Electrophoresis

Capillary electrophoresis (CE) is a special case of using an electrical field to separate the components of a mixture [98]. CE is a powerful clinical diagnostic tool for profiling, screening, and detecting drugs, carbohydrates, lipids, enzymes, proteins, and nucleic acid [99]. Four capillary electrophoresis methods [88,89,90,91] were developed for chiral determination of drugs. Method developed by Maier *et al*. [88] is the most sensitive method among capillary electrophoresis methods.

2.4. Radioreceptor Assay

Radioreceptor analysis method was developed by Taguchi et al. [100]. This was performed by pharmacokinetic analysis of receptor binding following single, oral dose of tamsulosin (0.4mg) in a placebo-controlled, single-blind, randomized, three-way cross-over study. This technique is effectively independent of knowledge of the chemical identity of drug metabolites and evaluates the parent compound and all of its metabolites according to their relative contribution to receptor binding [100].

3. Conclusion

Metabolic and regulatory processes mediated by biological systems are sensitive to stereochemistry, and different responses can be often observed when comparing the activities of pair of enantiomers. Thus, regulatory authorities encourage the pharmaceutical industries to provide single enantiomer of drugs, although most of them were commercialized as racemates. Nowadays, the situation has definitely changed, as technical advances permit production of many single enentiomer on a commercial scale. Thus there is clear need for such kind of review of analytical methods of drugs as well as separation of isomers in different matrices [101].

In general, the LOD is taken as the lowest concentration of an analyte in a sample that can be detected, but not

necessarily quantified, under the stated conditions of the test. The LOQ is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test. This is the reason here it is important to discuss about these parameters [102].

Reactions of both the isomers also vary and with post/pre column derivatization and using liquid chromatography the spectrum of analytical methods for separation of isomers can be further increased. In this way various analytical methods for the determination of tamsulosin and its isomers are discussed. The presented review can be useful for the researchers involved in the development of new analytical methods or formulations.

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