Indirect spectrofluorimetric determination of omeprazole by its quenching effect on the fluorescence of Tb^{3+}-1,10-phenanthroline complex in presence of bis (2-ethylhexyl) sulfosuccinate sodium in capsule formulations

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ABSTRACT

Purpose: Omeprazole (OMZ) is a substituted benzimidazole, which is used in the treatment of gastric acid related disorders. The aim of this study was the development and validation of a rapid, simple and reliable fluorimetric method for determination of OMZ in pharmaceutical formulations based on fluorescence quenching of Tb^{3+}-1, 10-phenanthroline complex.

Method: For the determination of OMZ, aliquots of Tb^{3+}, bis (2-ethylhexyl) sulfosuccinate sodium (AOT), 1,10-phenanthroline (phen) solutions (in optimal concentrations), aliquots of working OMZ solution and Tris-HCl buffer (pH 7.0) solution were added to 5 mL volumetric flasks. The mixture was then diluted with distilled water and allowed to stand for 30 min and the fluorescence intensity was then measured at 545 nm using an excitation wavelength of 300 nm. Matrix systems of OMZ (OMZ capsules with a nominal of 20 mg) were prepared by powdering and mixing the contents of ten capsules of OMZ. A portion of 10.0 mg of this powder was then accurately weighed and dissolved in about 10 mL of 0.1 M NaOH solution and filtered into a 100 mL volumetric flask. The residue was washed several times with water and solution was diluted to the mark. A suitable aliquot of this solution was applied for fluorimetric determination of OMZ. The recovery assay was carried out using the same procedure by addition of known amounts of OMZ.

Results: It was found that the fluorescence intensity of Tb^{3+}-1, 10-phenanthroline complex can be greatly quenched by omeprazole in the presence of AOT. Under optimal conditions, the quenched fluorescence intensity was found to be proportional to the concentration of omeprazole in the range of 0.05-10 µg/mL. The detection limit was 0.016 µg/mL. The relative standard deviation values for 6 replicated determinations of 0.3 and 1.5 µg/mL of OMZ were 3.5 and 1.5 %, respectively, The RSD of intraday was 2.6 and that of interday was 3.4 % for 4 and 2 µg/mL of OMZ, respectively.

Conclusion: Based on the obtained results, a simple, rapid and selective spectrofluorimetric method was developed for determination of omeprazole in its capsule formulations with excellent reproducibility and allowed the interference-free determination of OMZ in real samples.

Keywords: Sensitized fluorescence, Omeprazole, Terbium, Fluorescence quenching

INTRODUCTION

Omeprazole (OMZ) (figure 1) (5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl) methyl] sulfinyl]-1H-benz-imidazole), which is used in the treatment of gastric acid related disorders (1). It is descomposed in acid media to yield two main products, i.e. sulphonamide and sulphenic acid. OMZ has also been found to be unstable in neutral and weak alkaline media but is stable in strong alkaline solutions where the maximum stability is at pH 11.

Several high-performance liquid chromatography (HPLC) methods with ultraviolet detection and electrochemical detection (2-5), liquid chromatography coupled with tandem mass spectrometry (6), spectrophotometry (7-10), polarography (11-13), voltammetry (14), capillary electrophoresis (15) and thin-layer chromatography (16) methods

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have been developed for determination of omeprazole in different samples. However these methods suffer from a number of limitations such as complex automated sample preparation system (4), liquid–liquid or uneconomical solid-phase extraction (SPE) (2-6), inconvenient chromatography (2), long analysis times (3), or the use of toxic halogenated solvents during sample preparation (3).

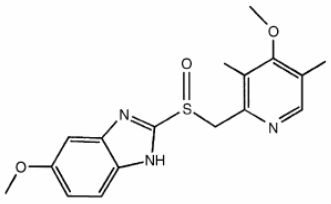

Figure 1. Structure of omeprazole.

Because of the high sensitivity and selectivity, and being rapid and simple, spectrofluorimetric methods have been widely used for determination of a wide range of pharmaceuticals with the advantages that in most instances, derivatization is not required, and that these methods are less sensitive to matrix effects than other analytical techniques (17, 18).

Rare-earth ions have luminescence characteristics such as narrow spectral width, long luminescence lifetime and large stocks shift. Therefore, the rare earth Tb^{3+} is often used as a fluorescence probe for determination of some substances because of the high fluorescence quantum efficiency of the terbium (III) chelates (18, 19).

A previous study (20) demonstrated that Tb^{3+}-1,10-phenanthroline (phen) complex had a strong intrinsic fluorescence of Tb^{3+} and since it was found that its fluorescence could be quenched by OMZ, a novel method for determination of OMZ was developed. To the best of our knowledge, this is the first attempt to determine OMZ in capsules by spectrofluorimetry.

MATERIALS AND METHODS

Reagents

All reagents and solvents were analytical grades and used without further purification. Doubly distilled water was used throughout this work. Two commercial OMZ products were purchased from a local pharmacy.

A 10^{-2} M terbium (Ш) solution was prepared by dissolving the appropriate amount of terbium (Ш) chloride hexahydrate ($TbCl_3$. 6 H_2O) (Acros Organics, USA) in doubly distilled water and stored in a polyethylene containers to avoid memory effects of terbium adsorbed on glass vessels.

OMZ powder was provided by Exir pharmaceutical company (Lorestan, Iran). A stock standard solution of 100 µg/mL was prepared by dissolving 10.0 mg of OMZ in approximately 10 mL of 0.1 M sodium hydroxide and was diluted to the mark in 100 mL volumetric flask with water.

A 10^{-2} M stock solution of 1, 10-phenanthroline (Fluka, Switzerland) was prepared in 10 mL ethanol and was diluted to the mark in 100 mL volumetric flask with doubly distilled water. A 10^{-2} M solution of bis (2-ethylhexyl) sulfosuccinate sodium (AOT) (Fluka, Switzerland) solution was prepared by dissolving the appropriate amount of AOT in doubly distilled water. Also aqueous solutions of N-cetyl-N,N,N-trimethylamonium bromide (CTAB), polyoxyethylene lauryl ether (Brij-35), sodium dodecyl sulfate (SDS), Triton X-100, hydrochloric acid, sodium hydroxide, α and β-cyclodexetrin (all were obtained from Merck) were prepared.

A 0.05 M Tris-(hydroxymethyl) aminomethan-hydrochloric acid (Tris- HCl) buffer solution was prepared by dissolving a desired amount of Tris-base (Merck) in 90 mL of water, adjusting the pH to 7.0 with HCl and making up the volume to 100 mL with water. Working standard solutions were prepared daily by successive dilution of the stock standard with water.

Apparatus

Fluorescence spectra and intensity measurements were performed using a Shimadzu RF-540 spectrofluorimeter (Kyoto, Japan) equipped with a 150 W xenon lamp, using 1.0 cm quarts cell. The excitation and emission monochromator band-widths were 10 nm. The excitation wavelength was set at 300 nm and the fluorescence was measured using the peak height at 545 nm. All measurements were performed at 25 ± 0.1 ºC using a thermostated cell holder and a thermostatically controlled water bath (Rikakika, Japan). The pH of solutions was measured using Metrohm model 654 pH meter (Herisau, Switzerland).

Methods

All measurements were corrected for the background fluorescence of blank which was taken as the solution containing all reagents except OMZ. Optimization of terbium sensitized fluorescence was investigated by variation of the pH or the concentration of one of the components while the remaining factors were kept constant.

Experimental procedure

For determination of OMZ, the analytical procedure which was used to construct the calibration graph was as follow: to 5 mL

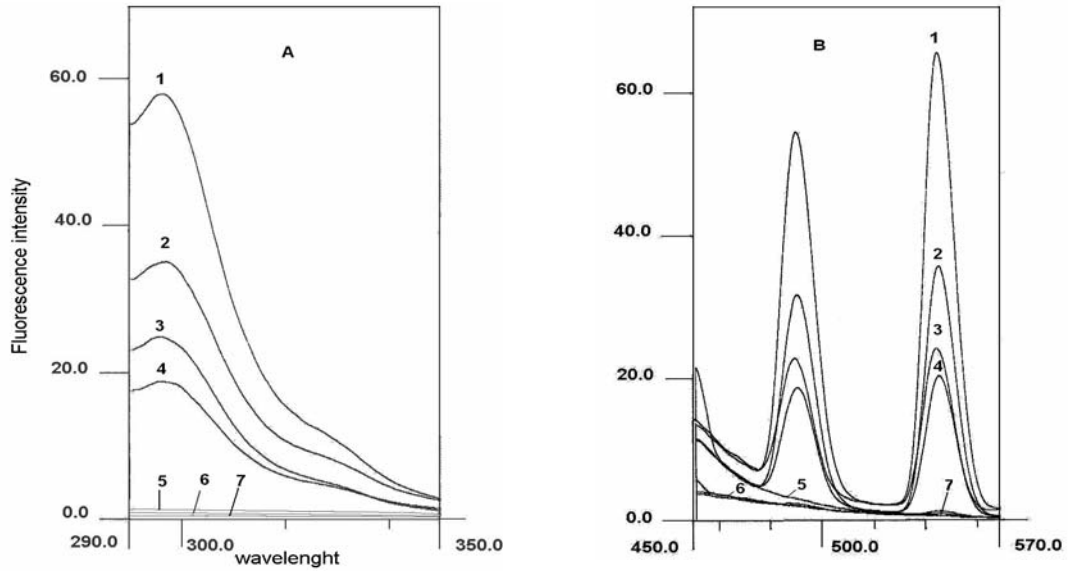

Figure 2. Terbium-sensitized fluorescence excitation (λ_{em} = 545 nm) (A) and emission (λ_{ex} = 300 nm) (B) spectra: (1) Tb-phen-AOT; (2) Tb-phen; (3) Tb-phen-OMZ; (4) Tb-phen-AOT-OMZ; (5) Tb^{3+}; (6) OMZ; (7) AOT. Conditions: $[Tb^{3+}] = 2\times10^{-4}$ M, [OMZ] = 2 µg/mL, [AOT] = 10^{-4} M, (pH = 7.0).

volumetric flasks, 1 mL of 1×10^{-3} M Tb^{3+} solution, 50 µL of 1×10^{-2} M AOT solution, 0.5 mL of 1×10^{-3} M phen solution, aliquots of working OMZ solution and 2 mL of 0.05 M Tris-HCl buffer (pH 7.0) solution were added. The mixture was then diluted to the mark with distilled water and allowed to stand for 30 min. The final OMZ concentration was in the range of 0.05-10 µg/mL. The solutions were thermostated at 25 ± 0.1 ºC and the fluorescence intensity was measured at 545 nm using an excitation wavelength of 300 nm against a blank solution. Both emission and excitation slits were set at 10 nm. The quenched fluorescence intensity of Tb^{3+}-phen–AOT by OMZ was represented as ΔI_f (%) = $(I_0–I_f)/I_0 \times 100$ in which I_f and I_0 were the intensities of the systems with and without OMZ, respectively.

Pharmaceutical preparation

Ten capsules of OMZ were weighed in order to find the average mass of each capsule. Then the contents were powdered and mixed. A portion of 10.0 mg of this powder was accurately weighed and dissolved in about 10 mL of 0.1 M NaOH solution and filtered into a 100 mL volumetric flask. The residue was washed several times with water and solution was diluted to the mark. A suitable aliquot of this solution was taken for fluorimetric determination of OMZ. The recovery assay was carried out using the same procedure by addition of known amounts of OMZ.

RESULTS AND DISCUSSION

Fluorescence spectra

Fluorescence excitation and emission spectra of (1) Tb-phen-AOT, (2) Tb-phen, (3) Tb-phen-OMZ, (4) Tb-phen-AOT-OMZ, (5) Tb^{3+}, (6) OMZ and (7) AOT systems at pH 7.0 are shown in figure 2. From spectra 5 (B) in figure 2, it may be found that almost no characteristic fluorescence of Tb^{3+} was observed in the Tb^{3+} system. It was found that after the excitation of 300 nm, the Tb^{3+}-phen system (3) emitted the characteristic fluorescence of Tb^{3+} ion with the emission peaks of 490 and 545 nm, which correspond to $^5D_4\rightarrow{}^7F_6$ and $^5D_4\rightarrow{}^7F_5$ transitions of Tb^{3+}, respectively. The addition of OMZ could quench fluorescence intensity of Tb^{3+}-phen system. However, in the presence of AOT, the fluorescence of this system was greatly quenched by OMZ, which indicated that there was interaction between OMZ, AOT and Tb^{3+}-phen. Therefore the Tb^{3+}-phen-AOT system was utilized in the assays of OMZ. Since the quenched fluorescence intensity at 545 nm was higher, this wavelength was chosen to detect the fluorescence intensities throughout all the experiments.

Factors affecting the fluorescence intensity of the system

The effect pH on the quenched fluorescence intensity of the Tb-phen-OMZ-AOT system was investigated in the pH range of 4.5-10.0 (figure 3). The results indicated that when the Tb-phen complex was more stable, OMZ had little effect

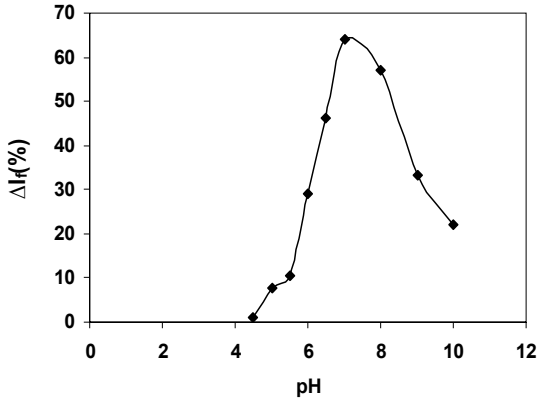

Figure 3. Effect of pH. Conditions: phen, 2 ×10^{-4} M; Tb^{3+}, 10^{-4} M; AOT, 10^{-4} M; OMP, 2 μg/mL.

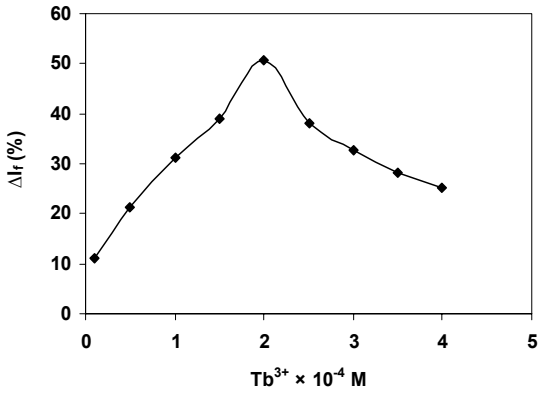

Figure 4. Effect of Tb^{3+} concentration. Conditions: phen, 2 ×10^{-4} M; AOT, 10^{-4} M; OMP, 2 μg/mL, Tris-HCl, 0.02 M (pH = 7.0).

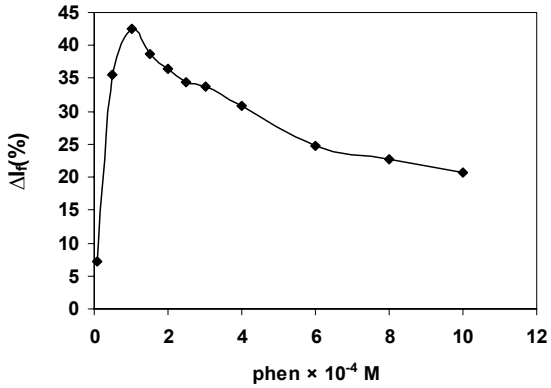

Figure 5. Effect of phen concentration. Conditions: Tb^{3+}, 2 ×10^{-4} M; AOT, 10^{-4} M; OMP, 2 μg/mL; Tris-HCl, 0.02 M (pH = 7.0).

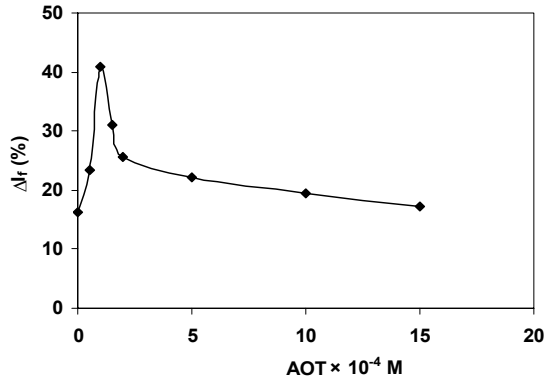

Figure 6. Effect of AOT concentration. Conditions: Tb^{3+}, 2 ×10^{-4} M; phen, 10^{-4} M; OMP, 2 μg/mL; Tris-HCl, 0.02 M (pH = 7.0).

on the complex (in the pH range of 2.0-5.5), and the quenched fluorescence intensity of the system reached a maximum when pH was 7.0. At higher pH (pH >7.0) the intensity decreased due to the precipitation of terbium hydroxide.

The results of the effect of the concentration of Tb^{3+} are shown in figure 4. The quenched fluorescence intensity of the system reached a maximum when Tb^{3+} concentration was 2×10^{-4} M. Therefore, 2×10^{-4} M of Tb^{3+} was chosen for further investigation.

The effect of phen concentration on the fluorescence intensity of Tb^{3+}-phen-AOT-OMZ system was studied (see figure 5), and was found that the quenched fluorescence intensity of Tb^{3+}-phen-AOT-OMZ system reached a maximum when the concentration of phen was 1×10^{-4} M.

The effects of the following surfactants and cyclodextrins (CDs) on the fluorescence intensities were tested. The ΔI_f (%) for AOT, sodium dodecyl sulphonate (SDS), cetyltrimethylammonium bromide (CTAB), Triton X-100, α-CD, β-CD and Brij 35 were 51.1, 43.7, 27.8, 18.6, 37.5, 25 and 18.4, respectively. The ΔI_f (%) of the system without surfactants was 16.2, which was the lowest in above systems. This indicated that addition of surfactants and/or CDs increase the quenching effect of OMZ on the fluorescence of Tb^{3+}-phen complex. The results showed that AOT had the best quenching effect on the fluorescence intensity of the system. The main reasons seem to be its negative charges and little steric hindrance. The effect of the AOT concentration was studied and is shown in figure 6. It was found that the ΔI_f (%) of this system reached a maximum when the concentration of AOT was 1×10^{-4} M.

The influence of the order of addition on the fluorescence intensity of this system was investigated and it was found that the best order of addition was Tb^{3+}-AOT-phen-OMZ-Tris-HCl and this order was selected for further investigations. Under optimal condition, the effect of time on the

Table 1. Tolerance limits of various interferents in the determination of 2 μg/mL of OMZ

Substances	Interferent-to-analyte ratio[(a)]	Change of ΔI_f (%)
Mannitol	60:1	-4.9
Lactose anhydrous	13:1	-3.8
Maize starch	10:1	3.3
Macrogol (PEG 6000)	14:1	1.7
Sodium carboxymethyl cellulose (NaCMC)	7:1	-3.7
Gelatin	56:1	-1.4
Povidone (PVP 25000)	7:1	2.5
Sodium laurylsulfate (SLS)	7:1	-6.3
Hyprolose (HPC)	4:1	2.6
Hypromellose phthalate (HPMC phthalate)	0.4:1	-7.0
Cellulose microcrystalline	0.7:1	-2.5
Magnesium stearate	0.4:1	-3.1
Disodium hydrogen phosphate dihydrate	0.07:1	5.1

[(a)] Interferent-to-analyte ratio is in final solutions.

Table 2. Determination of OMZ in pharmaceutical preparations (20 mg capsules)

	EXi PRAZOLE ® 20	OMEPRAZOLE 20
Found ±s (mg per capsule)[a]	19.71 ± 0.17 t = 3 (4.3)[c] (n = 3)	21.3 ± 1.1 t = 2 (4.3) (n = 3)
Recovery ± s (%) [b]	98.5 ± 0.84	106.3 ± 5.6

[a] Standard deviation (average of three determination).
[b] Recovery is calculated from the content reported by laboratory.
[c] The figure in parentheses is the tabulated t value at 95% confidence level.

Table 3. Recoveries of OMZ added to the pharmaceutical preparations

Amount added (μg/mL)[a]	Amount found (μg/mL)[b]	
	EXi PRAZOL ® 20	OMEPRAZOLE 20
4.0	4.1 ± 0.12, (102.5 ± 3.1)[c]	-
6.0	6.1 ± 0.0.21, (101.7 ± 3.3)	-
8.0	8.2 ± 0.34, (102.5 ± 4.3)	-
2.0	-	1.9 ± 0.058, (95.0 ± 2.9)
4.0	-	4.3 ± 0.098, (107.5 ± 2.5)
6.0	-	6.4 ± 0.18, (106.7 ± 3.0)

[a] The given values are concentration in prepared samples.
[b] Average of three determinations ± S.D.
[c] Recovery (%).

fluorescence intensity was studied. After addition of all reagents, oscillated for 5 min and allowed to stand for 25 min, the ΔI_f (%) reached a maximum and remained basically stable for over 1 h without having any significant effects on the results.

Analytical figures of merit

By using the optimized conditions described above, a spectrofluorimetric method was developed for determination of OMZ in the capsules. The calibration graph (n = 12) was found to be linear in the range of 0.05 to 10 μg/mL for OMZ and its equation was ΔI_f (%)= 6.57 C + 15.27, where ΔI_f (%) is the quenched fluorescence intensity of Tb^{3+}-phen-AOT by OMZ and C is the concentration of OMZ expressed in μg/mL.

The limit of detection was calculated as $3S_b/m$ (where S_b is standard deviation of the blank and m is slope of the calibration graph) and it was found to be 0.016 μg/mL.

In order to study the precision of the proposed method **(**repeatability), series of six solutions of 0.3 and 1.5 μg/mL of OMZ were measured on the same day. By applying the ICH definition, the relative standard deviation (RSD) for six analyses were 3.5 and 1.5 %, respectively. To assess the day-to-day precision (intermediate precision),

repeated analyses of 4 and 2 µg/mL of OMZ (six analyses) were performed over two weeks and interday RSD were 2.6 and 3.4 %, respectively.

The selectivity of the method was investigated and no interferences were observed between OMZ and common excipients for capsules formulations. The interference of typical excipients (21) was studied by addition of increasing concentration of these compounds to solution of 2 µg/mL of OMZ until variation greater than 5 % in analytical intensity was achieved. As shown in the Table 1, most excipients except disodium hydrogen phosphate dehydrate and hypromellose phthalate (due to interaction of phosphate and phthalate by terbium, [22, 23]) either had no effect or had little effect on the determination of OMZ under the permission of ± 5 % relative error. Hence selectivity achieved by the proposed method is good and it is possible to determine OMZ in the presence of the excipients.

Application

OMZ was satisfactorily analyzed in two commercial products of Iranian pharmaceutical market (OMZ capsules with a nominal of 20 mg) by terbium sensitized fluorescence method. According to the characteristics of the fluorescence spectra of these two preparations, there was no interference from the excipients. Table 2 shows the results for triplicate analyses. Statistical analysis of the assay results showed satisfactory accuracy and precision of the proposed method with no significant differences between certified and experimental results ($P < 0.05$, Table 2).

Recovery of OMZ from pharmaceutical preparations spiked with different amounts of this drug was between 95 % and 107.5 %. (Table 3). The RSDs of the method for triplicate analyses of capsule samples containing different brands of OMZ were 2.3 - 4.1%.

Mechanism of Interaction of the system

As it can be found from figure 1, in the presence of AOT, OMZ quenches the fluorescence of Tb^{3+}-phen system, and there is an interaction among OMZ, AOT and Tb^{3+}-phen which may be a large complex of Tb^{3+}-phen-AOT-OMZ in this system. A previous investigation (20) has shown that Tb^{3+} can combine with phen to form 1:3 complexes with positive charge, which emits strong characteristic fluorescence of Tb^{3+}. This is attributed to intramolecular energy transfer between phen and Tb^{3+}. On the other hand, OMZ has coordination ability towards some cations (10). Structural formulae of OMZ, showed that metal chelates can be formed between the imidazole-NH group, the oxygen of the sulfur dioxide side chain, and the N of the pyridine to yield a six-membered ring. Therefore, OMZ may coordinates with Tb^{3+} in Tb-phen system. On the other hand, AOT with negative charges can react with Tb^{3+}-phen complex through electrostatic forces. Therefore, both AOT and OMZ can react with Tb^{3+}-phen complex, which weaken combination between Tb^{3+} and phen resulting in the fluorescence quench of Tb^{3+}-phen system.

CONCLUSIONS

The official analytical method of OMZ in BP is the non-selective titrimetic method with standard NaOH (24). The conventional UV method (9) suffer from interference due to UV absorbing compounds in the determination of OMZ.

On this basis, of results of this study a new spectrofluorimetric method was developed for determination of OMZ in real samples based on terbium sensitized fluorescence. The proposed method is very simple, precise, and rapid was easily applied to determination of OMZ in capsules with excellent reproducibility and allowed the interference-free determination of OMZ in real samples.

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REFERENCES

1. Howden CW. Clinical pharmacology of omeprazole. Clin Pharmacokinet 1991; 20: 38-49.
2. Lagerström PO, Persson BA. Determination of omeprazole and metabolites in plasma and urine by liquid chromatography. J Chromatogr B 1984; 309: 347-356.
3. Kobayashi K, Chiba K, Sohn DR, Kato Y, Ishizaki T. Simultaneous determination of omeprazole and its metabolites in plasma and urine by reversed-phase high-performance liquid chromatography with an alkaline-resistant polymer-coated C_{18} column. J Chromatogr B 1992; 579: 299-305.
4. Grundevik I, Jerndal G, Balmer K, Persson BA. Fully automated gradient elution liquid chromatographic assay of omeprazole and two metabolites. J Pharm Biomed Anal 1986; 4: 389-398.
5. Sluggett GW, Stong JD, Adams JH, Zhao Z. Omeprazole determination using HPLC with coulometric detection. J Pharm Biomed Anal 2001; 25: 357-361.
6. Yin OQP, Lam SSL, Lo CMY, Chow MSS. Rapid determination of five probe drugs and their metabolites in human plasma and urine by liquid chromatography/tandem mass spectrometry:

Application to cytochrome P450 phenotyping studies. Rapid Commun Mass Spectrom 2004; 18: 2921-2933.
7. Sastry CSP, Naidu PY, Murty SSN. Spectrophotometric methods for the determination of omeprazole in bulk form and pharmaceutical formulations. Talanta 1997; 44: 1211-1217.
8. Wahbi AM, Abdel-Razak O, Gazy AA, Mahgoub H, Moneeb MS. Spectrophotometric determination of omeprazole, lansoprazole and pantoprazole in pharmaceutical formulations. J Pharm Biomed Anal 2002; 30: 1133-1142.
9. Özaltin N, Kocer A. Determination of omeprazole in pharmaceuticals by derivative spectroscopy. J Pharm Biomed Anal 1997; 16: 337-342.
10. Salama F, El-Abasawy N, Abdel Razeq SA, Ismail MM. F, Fouad MM. Validation of the spectrophotometric determination of omeprazole and pantoprazole sodium via their metal chelates. J Pharm Biomed Anal 2003; 33: 411-421.
11. Özaltin N, Temizer A. Differential pulse polarographic determination of omeprazole in pharmaceutical preparations. Electroanalysis 1994; 6: 799-803.
12. Oelschlaeger H, Knoth H. Polarographic analysis of omeprazol formulations. Pharmazie 1998; 53: 242-/244.
13. McClean S, OKane E, Ramachandran, VN, Smyth WF. Differential pulse polarographic study of the degradation of H+/K+ ATPase inhibitors SK&F 95601 and omeprazole in acidic media and the subsequent reactions with thiols. Anal Chim Acta 1994; 292: 81-89.
14. Pinzauti S, Gratteri P, Furlanetto S, Mura P, Dreassi E, Phan-Tan-Luu R. Experimental design in the development of voltammetric method for the assay of omeprazole. J Pharm Biomed Anal 1996; 14: 881-889.
15. Berzas Nevado JJ, Castañeda Peñalvo G, Rodríguez Dorado RM. Method development and validation for the separation and determination of omeprazole enantiomers in pharmaceutical preparations by capillary electrophoresis. Anal Chim Acta 2005; 533:127-133.
16. Tunalier AKDZ, Tuncel M. TLC densitometric determination of omeprazole in pharmaceutical preparations. Pharmazie 1998; 53: 272-273.
17. Han Y, Wu X, Yang J, Sun S. The fluorescence characteristic of the yttrium-norfloxacin system and its analytical application. J Pharm Biomed Anal 2005; 38: 528-531.
18. Tong C, Hu Z, Liu W. Sensitive determination of DNA based on the interaction between norfloxacin-Tb^{3+} complex and DNA. J Agric Food Chem 2005; 53: 6207-6212.
19. Tong CL, Xiang GH, Huang DJ, Liu WP. Determination of ofloxacin by the terbium(III) ion fluorescence probe sensitized by the surfactant. Chin J Anal Chem 2004; 32: 619-621.
20. Kang JG, Kim TJ, Kang HJ, Kang SK. Crystal structures and luminescence properties of $[Eu(ODA)\cdot(phen)\cdot 4H_2O]^+$, $[Tb(ODA)\cdot(phen)\cdot 4H_2O]^+$ and $[Tb(ODA)_3]^{3-}$ (ODA: oxydiacetate, phen: 1,10-phenanthroline). J Photochem Photobiol A: Chem 2005; 174: 28-37.
21. http://emc.medicines.org.uk/emc/assets/c/html/Display and www. 247-pharmacy.com/buy/prilosec. .php , accessed on 19 Oct 2008.
22. Casas-Hernández AM, Paz Aguilar-Caballos M, Gómez-Hens A. Application of Time-Resolved Luminescence Methodology to the Determination of Phthalate Esters. Anal lett 2003; 25: 1017-1027.
23. Fengshan Y, Lin L, Fang C. Determination of adenosine disodium triphosphate using prulifloxacin–terbium (III) as a fluorescence probe by spectrofluorimetry. Anal Chim Acta 2008; 610: 257–262.24. British Pharmacopoeia, B.P. 1993 (Addendum 1995), HMSO, London, p. 1590.