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A novel chemiluminescence quenching method for determination of sulfonamides in pharmaceutical and biological fluid based on luminol–Ag(III) complex reaction in alkaline solution

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A novel chemiluminescence (CL) quenching method for the determination of sulfonamides is proposed. The CL reaction between Ag(III) complex $[Ag(HIO_6)_2]^{5-}$ and luminol in alkaline solution was investigated. The quenching effect of sulfonamides on CL emission of $[Ag(HIO_6)_2]^{5-}$–luminol system was found. Quenching degree of CL emission was proportional to sulfonamide concentration. The effects of the reaction conditions on CL emission and quenching were examined. Under optimal conditions, the detection limits (s/n = 3) were 7.2, 17 and 8.3 ng/mL for sulfadiazine, sulfameter, and sulfadimethoxine, respectively. The recoveries of the three drugs were in the range of 91.3–110% with RSDs of 1.9–2.7% for urine samples, and 106–112% with RSDs of 1.6–2.8% for serum samples. The proposed method was used for the determination of sulfadiazine at clinically relevant concentrations in real urine and serum samples with satisfactory results.

Keywords: chemiluminescence; quenching effect; Ag(III) complex; sulfonamides; luminol: injection; biological fluid

Introduction

Sulfonamides are a group of antibacterial agents commonly used in veterinary practice to prevent infections in livestock, to treat diseases, and to promote growth.[1] The sensitivity of sulfonamides to the environment affects their activity in particular fluids and tissues, and also the ability of laboratories to standardize the minimum inhibitory concentrations necessary *in vivo* to inhibit specific cultured bacteria. These drugs also frequently induce various side effects.[2] Many of them become toxic even when slightly overdosed. In human blood, concentrations above 200 μg/mL may cause adverse effects, therefore the maximum sulfonamide blood level should not exceed this concentration. This requires high performance, selective, and sensitive methods for their determination in medicinal forms and biological fluids. Therefore, development of analytical methods of sulfonamides in biological samples is of considerable importance.

A series of analytical techniques has been proposed for the determination of sulfonamides, such as dead-stop titration,[3] spectrophotometry,[4,5] fluorimetry,[6] electrochemistry,[7] and immunoassay[8–10] as well as oscillating chemical method.[11] Chromatographic methods (including gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS)) were widely used for the determination of sulfonamide residues in foods in recent years.[12,13] Chemiluminescence (CL) is known to be a powerful analytical technique that has high sensitivity, wide linear range, and simple instrumentation; it has been applied for biomedical, pharmaceutical, clinical analysis.[14,15] In the last few years, CL-based detection using different CL systems has become quite a useful detecting tool in liquid chromatography for clinical, pharmaceutical, environmental, and food analysis.[16] Several CL methods were reported for the determination of sulfonamides in pharmaceutical and biological samples.[17–21] An analytical method consisting of flow injection (FI) sampling and CL detection for determination of sulfamethoxazole (SMZ) was described based on the CL reaction of $KMnO_4$–Na_2SO_3–SMZ system with the limit of detection (LOD) of 300 ng/mL.[17] A CL quenching method with $KMnO_4$ was reported for determination of SMZ in compound SMZ tablets.[18] Based on formaldehyde-enhancing CL in the oxidation of sulfa drugs by soluble manganese(IV), a new CL method to determine sulfa drugs such as SMZ, sulfadiazine, and sulfaguannidine with FI technique was developed with the LOD of 20–30 ng/mL.[19] A simple, sensitive, and selective FI-CL method for the determination of sulfadiazine in compound naristillae was investigated based on the CL reaction of sulfadiazine, formaldehyde, and potassium permanganate in polyphosphate acid medium with the LOD of 50 ng/mL.[20] A CL flow injection analysis (FIA) system was applied to the determination of sulfadiazine using

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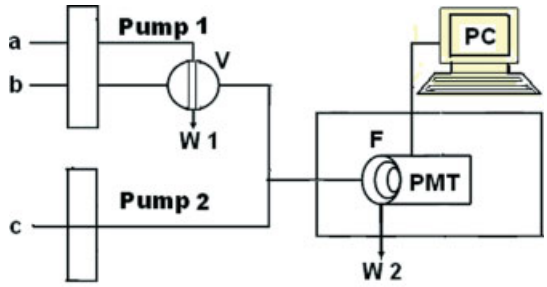

Figure 1. Schematic diagram of flow injection CL analysis system. Pump 1 and Pump 2 – peristaltic pumps; V – sampling inlet valve; F – flow cell: a flat spiral-coiled colourless glass tube (i.d. 1.0 mm, total diameter of the flow cell 3 cm, without gas between loops); PMT – photomultiplier tube; W – waste; (a) $[Ag(HIO_6)_2]^{5-}$ solution, (b) luminol alkaline solution, (c) sulfonamides solution.

bis[2,4,6-trichlorophenyl]oxalate as CL precursor, H_2O_2 as an oxidant, imidazole as a catalyst, and fluorescamine as the fluorescent derivatizing agent with the limit of quantification (LOQ) of 379 ng/mL.[21]

In our previous work, a new CL reaction system with Ag(III) complex in acidic medium was developed for the determination of fluoroquinolones.[22,23] Shi *et al*. reported a new CL method for the determination of cortisol based on cortisol-enhanced effect on CL reaction of Ag(III) complex with luminol.[24] We found that CL emission of Ag(III) complex–luminol in alkaline medium could be quenched by sulfonamides. The CL quenching degree was linear with the concentration of sulfonamide. A new and sensitive CL quenching method was developed, and was applied for the determination of any test sulfonamides in urine and serum.

Experimental

Apparatus

The FI system, as shown in Figure 1, is an IFFM-D FICL analysis system (Xi'an Remex Electronic Science Tech Co. Ltd, Xi'an, China) consisting of two peristaltic pumps working at a constant flow rate (60 rpm, 3.0 mL/min) and a six-way injection valve with a sample loop (120 μL), which is automatically operated by a computer-equipped operation system of IFFM-D FIA. PTFE tubing (0.8 mm i.d.) was used to connect all components in the flow system. The flow cell was placed close to the window of the photomultiplier tube (PMT, operated at −800 V).

Reagents

Sodium periodate ($NaIO_4$, 99.5%) was purchased from Tianjin Kermel Chemical Reagent Company (Tianjin, China). Potassium peroxydisulfate ($K_2S_2O_8$, 99.5%) was purchased from Beijing Chemical Reagent Company (Beijing, China). Silver nitrate ($AgNO_3$, 99.8%) and potassium hydroxide (KOH, 82%) were purchased from Tianjin Damao Chemical Reagent Company (Tianjin, China). All chemicals were of analytical reagent grade and used without further purification, and deionized water was used throughout.

The Ag(III) complex, bis(hydrogenperiodato) argentate(III) complex anion ($[Ag(HIO_6)_2]^{5-}$), stock solution was prepared by oxidizing Ag(I) in the alkaline medium according to the known method.[25] The concentration of Ag(III) complex solutions prepared was determined accord to literature.[26]

Stock standard solution of sulfadiazine, sulfameter, and sulfadimethoxine (0.5 mg/mL) was prepared, respectively, by dissolving 25 mg sulfadiazine, sulfameter, and sulfadimethoxine in 5 mL of 0.01 M sodium hydroxide and diluting with deionized water to 50 mL and stored in refrigerator at 5 °C. The lower concentrations were prepared immediately prior to use.

Procedures

The investigation of the CL intensity-time profiles was performed with the static CL analysis. In a 10-mL calibrated flask, 0.1 mL luminol alkaline solution (3.2×10^{-8} M), 0.2 mL sulfonamide or 0.2 mL H_2O were mixed, then 1 mL 0.05 mM $[Ag(HIO_6)_2]^{5-}$ was injected into the reaction tube by a quantitative injector and the CL intensity was measured without stirring.

In the FI system, both luminol alkaline solution and sulfonamide solution were pumped through the flow lines (b) and (c), respectively, When the injection valve was switched to the position of injection $[Ag(HIO_6)_2]^{5-}$ solution through the flow lines (a) mixed with the mixture of luminol and sulfonamide solution, producing CL emission. The concentration of sulfonamide was quantified by the decrement of peak height of the CL signals.

Sample treatment

Urine and serum samples were provided by the Hospital of Hebei University. 1.0 g PbO_2 powder was added in 5.0 mL of blank urine, and followed by stirring for 10 min to eliminate urine acid, thiourea, and ascorbic acid, etc. After centrifugation for 10 min at 10 000 rpm, the supernatant was filtrated, then the filtrate was applied to a cation exchange column (4 cm × 1.2 cm) for clean-up. The clear liquid was diluted with deionized water to make different concentrations of sulfonamides in the linear range. The protein was removed by adding 4.0 mL 10% trichloroacetic acid (CCl_3COOH) in a centrifuge tube, which was shaken for 5 min, then centrifuged at 10 000 rpm for 10 min. The supernatant was diluted with deionized water to make different concentrations of sulfonamide in the linear range. The standard addition method was used to avoid matrix effects.

Results and Discussion

Characteristic of chemiluminescence

In order to get an idea of the reaction product generating CL, the CL spectra of $[Ag(HIO_6)_2]^{5-}$ – luminol system were recorded by Hitachi F-7000 fluorescence spectrophotometer (taken off lamphouse), as shown in Figure 2.

The CL emission was different with those of $[Ag(HIO_6)_2]^{5-}$—H_2SO_4 system.[22,23] It is seen that a CL peak at about 425 nm was observed under the low concentration of Ag(III), suggesting that the CL reactions shared a common emitting species. Like to H_2O_2, Ag(III)* could oxidate luminol to produce luminol free radical, which could be excited by Ag(III)* further.[24,27] However, the CL peak transferred slightly towards long wavelength with the increase of Ag(III) content. The mechanism of CL emission for the $[Ag(HIO_6)_2]^{5-}$ – luminol–KOH system is to be examined further.

Otherwise, the quenching effect of the drugs on CL emission that was observed is possible due to a part of $[Ag(HIO_6)_2]^{5-}$ being consumed for oxidation of sulfonamides. The CL intensity-time profiles of luminol–$[Ag(HIO_6)_2]^{5-}$ system and

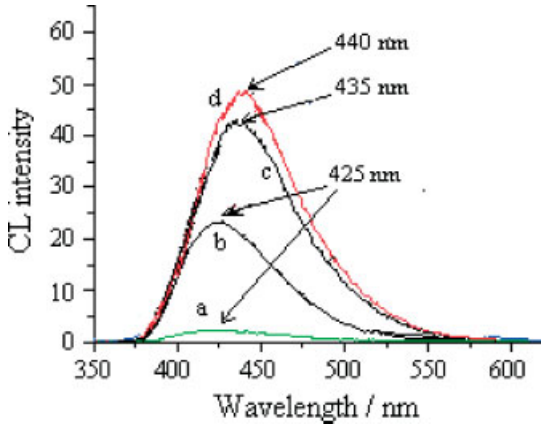

Figure 2. CL spectra of different systems in 0.15 M KOH medium. a: 0.69 mM Luminol–0.1 mMH_2O_2 system; b: 0.69 mM luminol–0.05 mM $[Ag(HIO_6)_2]^{5-}$ system; c: 0.69 mM luminol–1.1 mM $[Ag(HIO_6)_2]^{5-}$ system; d: 0.69 mM luminol–1.3 mM $[Ag(HIO_6)_2]^{5-}$ system.

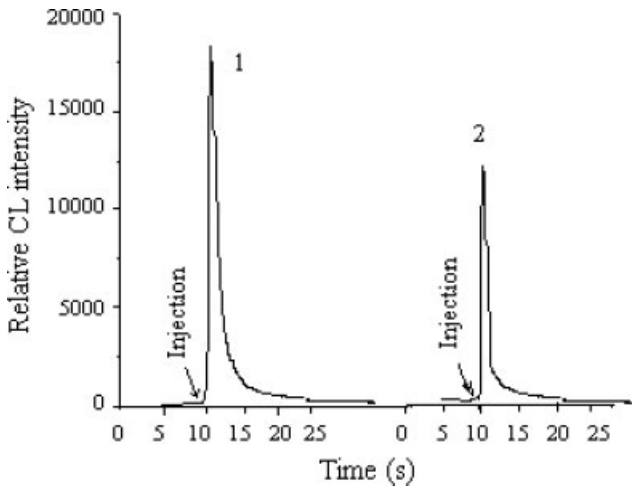

Figure 3. Chemiluminescence intensity time profiles for 3.2×10^{-8} M luminol in 0.15 M KOH solution and 0.1 mM $[Ag(HIO_6)_2]^{5-}$. Sulfadiazine: (1) 0, (2) 0.8 μg/mL.

luminol–$[Ag(HIO_6)_2]^{5-}$–sulfanilamides were observed by static injection method, as shown in Figure 3.

It is shown that the CL signal of luminol–$[Ag(HIO_6)_2]^{5-}$ system reached its maximum value only for 0.8 s and decayed quickly ($t_{1/2}$ = 1.2 s). The signal 2 was produced when the sulfanilamide was added, which reached its maximum signal only for 0.3 s and decayed quickly ($t_{1/2}$ = 0.4 s). It is clear that the CL method is sensitive enough and sulfanilamides have a strongly quenching effect on the luminol–$[Ag(HIO_6)_2]^{5-}$ CL reaction. Both sulfameter and sulfadimethoxine have similar CL profiles.

Effect of sample volume and flow rate

The role of sample volume and flow rate is critical. For instance, if the sample volume is too small or too large, the maximum CL could not be obtained. The highest emission was obtained when the injected sample volume was 120 μL. The CL intensity increased with increasing flow rate. A flow rate of 3.0 mL/min for all solutions was recommended because of greater precision and economy in the use of reagents.

Effect of alkaline medium

The kind and concentration of the alkaline used in the reaction has a very significant influence on the CL emission intensity. Several alkaline, such as the same concentration Na_2CO_3, $NaHCO_3$, Na_2CO_3-$NaHCO_3$, NaOH and KOH, were added in the same concentration luminol solution to test the effect of alkaline medium on the CL signal, respectively. The highest and most stable CL intensity was observed in KOH medium. The effect of KOH concentration on the relative CL intensity was investigated in the range of 0.01–0.40 M. The results show that relative CL intensity increased markedly in the absence of sulfadiazine with increasing KOH concentration up to 0.20 M, and increased in the presence of sulfadiazine with increasing KOH concentration up to 0.30 M. When KOH concentration of 0.15 M was used, the most quenching was obtained by 65%. Hence, 0.15 M KOH was used as the optimum concentration for further tests.

Effect of luminol concentration

The concentration of luminol has a very important effect on the relative CL intensity for the determination of sulfonamides. The dependence of the luminol concentration in the range of 8×10^{-9} to 2.5×10^{-7} M on the CL intensity was investigated for 400 ng/mL sulfadiazine. The results show that CL intensity increased obviously with increasing luminol concentration in the advance of sulfadiazine, and increased slightly in the presence of sulfadiazine. When the concentration of luminol was 1.5×10^{-7}, 2.0×10^{-7}, 2.2×10^{-7} M, the relevant quenching efficiency was 87.5, 88.2 and 84.6%. So 2.0×10^{-7} M luminol was selected as the optimum concentration for the next test.

Effect of $[Ag(HIO_6)_2]^{5-}$ concentration

In the CL systems, $[Ag(HIO_6)_2]^{5-}$ was used as an oxidant instead of H_2O_2. The $[Ag(HIO_6)_2]^{5-}$ concentration not only influenced the sensitivity, but also influenced the linear range for the assay. The influence of $[Ag(HIO_6)_2]^{5-}$ concentration on the CL signal was tested in the range of 0.01 to 0.4 mM. In the absence of sulfadiazine, the most CL intensity was reached when $[Ag(HIO_6)_2]^{5-}$ concentration was in the range of 0.05–0.12 mM, and decreased markedly when over 0.12 mM. In the presence of sulfadiazine, CL intensity was quenched markedly, and the most quenching efficiency (86.5%) was achieved when used 0.05 mM $[Ag(HIO_6)_2]^{5-}$, which was selected as optimum concentration.

Analytical performance of CL systems

The interfering effects from foreign species were investigated. The tolerance content was defined as the amount of coexisting species that produced an error not exceeding ±5% in the determination of sulfonamides; the results are listed in Table 1. The data show that there were few interferences. However, since the serum sample has higher concentration of these proteins than the urine sample, trichloroacetic acid should be added to each serum sample to remove the proteins mentioned above before determination. Standard addition method was used in sample analysis to eliminate the matrix influence further.

In the initial experiment, the CL quenching effect of sulfadiazine in the range of 0.04–4.0 μg/mL is shown in Figure 4. Under the optimized conditions, the linearity was evaluated for the sulfonamides. The calibration graph in wide concentration range for the determination of sulfonamides consisted of three parts in

Table 1. Tolerable content of foreign species for quantitative determination

Foreign species	Tolerable concentration (μg/mL)		
	Sulfadiazine[a]	Sulfameter[b]	Sulfadimethoxine[c]
Polyglycol	80	100	89
Sodium	214	200	150
Amylum,	100	50	32
Dextrin	50	42	28
Glucose	2	2	5
Lactose	50	33	25
Sucrose	3	5	8
Ca^{2+}	10	5	7
Mg^{2+}	200	100	100
EDTA	200	135	120
Zn2+	20	11	12
Cu^{2+}	100	80	95
Co^{2+}	30	21	24
Ba^{2+}	5	3	3
Fe^{3+}	4	3	2
Vitamin C	0.2	1	0.2

[a] 0.16 μg/mL; [b] 0.12 μg/mL; [c] 0.16 μg/mL.

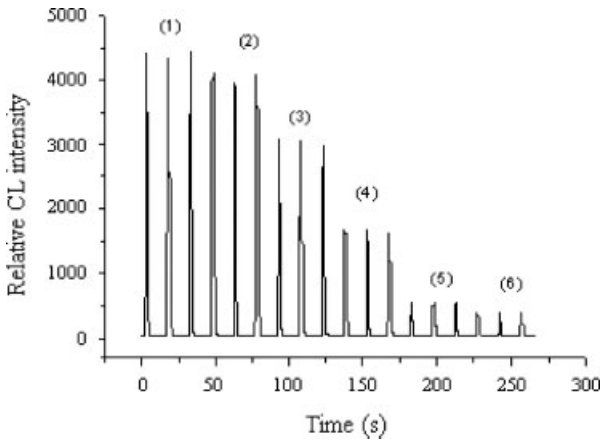

Figure 4. The CL quenching effect of sulfadiazine. $[Ag(HIO_6)_2]^{5-}$, 0.05 mM; KOH, 0.15 M; luminol, 2.2×10^{-7} M; sulfadiazine concentration: (1) 0, (2) 0.04 μg/mL, (3) 0.12 μg/mL, (4) 0.6 μg/mL, (5) 1.0 μg/mL, (6) 4.0 μg/mL.

order to improve the veracity. Linearities of calibration curve based on the difference (ΔI) between the CL intensities in the advance and presence of analyte towards its concentration (C) were investigated. The regression equations are given in Table 2, along with the detection limit and relative standard deviation (RSD).

The content levels of sulfonamides in human blood are usually maintained at approximately 50–100 μg/mL; otherwise, the content of sulfonamides in urine and serum is related to the sampling time after dosing.[28,29] Some or other regression equations could be selected through proper dilution in terms of concentration range in real urines.

For the broadest concentration range of 40–4000 ng/mL for sulfadiazine, 20–4000 ng/mL for sulfameter and 10–800 ng/mL for sulfadimethoxine, linearities of the calibration curve are poor; however, the linearities between ΔI and Lg C are better. The regression equations of the calibration curves can be shown as follows: $\Delta I = 1616$ Lg $C - 1875$ for sulfadiazine, 1210 Lg C – 1357 for sulfamete, $\Delta I = 1097$ Lg $C - 1527$ for sulfadimethoxine, and all the correlation coefficients (R^2) were $\geq$0.981. It can be seen that the linearity is acceptable based on the criteria ($R^2 \geq 0.98$) described by Green.[30]

The LOD was determined as the sample concentration that produces a peak with a height three times the level of baseline noise. The LOD was 7.2, 17, 8.3 ng/mL for sulfadiazine, sulfameter, and sulfadimethoxine, respectively, and the RSDs were in the range of 1.3–2.1%. The LOD of the proposed method is lower than those achieved with CL methods.[17–21] The high assay sensitivity allowed a high-fold dilution of the samples before analysis to avoid sample matrix effects.

It is indicated that the proposed CL quenching method has satisfactory linearity, sensitivity, and precision.

Sample analysis

The injection sample of sulfadiazine was a mixture which consists of ten bottle sulfadiazine injections selected from the same group randomly. The right amount of the sample solution was taken in a 100-mL flask and diluted with water. A proper sample solution was taken in a 50-mL flask as a working solution. Standard sulfadiazine solution was then added to the working solution and diluted with water. The sulfadiazine injections were analyzed using the standard addition method. The recovery was in the range of 94.7–104%. For an injection sample (labelled content: 1 g per 5 mL), the sulfadiazine content obtained using the proposed method was 0.98 g per 5 mL with RSD($n = 5$) of 1.8–2.2%, and that by using the Pharmacopoeia Method[3] was 0.97 g per 5 mL. The results obtained by the two methods were consistent. There was no significant difference between the labelled contents and the results obtained by the proposed method.

The proposed method was applied for the determination of sulfonamides. Human serum and urine samples were provided by the healthy volunteers without dose. Blank samples were diluted appropriately and treated according to the procedure described above. Standard addition method was used to avoid matrix effects. A known amount of the standards was added in urine samples to propose the recovery test. The results of recovery tests are listed in Table 3.

For spiked urine samples, the recoveries of the three drugs were in the range of 91.3–110% for sulfadiazine with RSDs of 2.1–2.2%, 102–103% for sulfameter with RSDs of 1.9–2.7%, and 102–103% for sulfadimethoxine with RSDs of 2.3–2.7%. For spiked serum samples the recoveries of the three drugs were in the range of 106–112% for sulfadiazine with RSDs of 2.4–2.8%, 108–110% for sulfameter with RSDs of 2.2–2.6%, and 104–111% for sulfadimethoxine with RSDs of 1.6–2.4%.

A patient was injected only with 2.5 g sulfadiazine; after 6 h, its urine and serum samples were taken, and treated using the procedure described above, diluted properly, then analyzed by the standard addition method. The obtained results are given in Table 4, along with the results obtained by the HPLC method.[13] The recoveries of sulfadiazine were in the range of 99.0–101% with RSDs of 2.0–2.5% for urine sample, and 98.5–100% with RSDs of 2.2–2.4% for serum sample. There was no significant difference between the results obtained by the proposed method and the office method.

Table 2. Analytical performance for determination of sulfonamides

Sulfonamides	Linear range (ng/mL)	Linear regression equation[a]	Correlation coefficient	RSD[b] (%)	LOD (ng/mL)
Sulfadiazine	40–120	$\Delta I = 757.3 + 6.163C$	0.9999	1.3	7.2
	120–1000	$\Delta I = 117.5 + 2.088C$	0.9975		
	1000–4000	$\Delta I = 2996 + 0.2623C$	0.9999		
Sulfameter	20–80	$\Delta I = 31.5 + 6.1536C$	0.9954		
	80–600	$\Delta I = 312 + 2.054C$	0.9962	1.6	17
	600–4000	$\Delta I = 1331 + 0.3026C$	0.9999		
Sulfadimethoxine	10–40	$\Delta I = -79.00 + 17.90C$	0.9913		
	40–400	$\Delta I = 575.7 + 3.3259C$	0.9930	2.1	8.3
	400–800	$\Delta I = 1579 + 0.7925C$	0.9975		

[a] ΔI, the difference between CL intensities in the presence and advance of analyte; [b] n = 11; [C] ng/mL.

Table 3. Recovery of sulfadiazine, sulfameter, and sulfadimethoxine in blank urine and serum samples

Analyte	Sample	Added (ng/mL)	Found (ng/mL)	Recovery (%)	RSD(n = 5) (%)
Sulfadiazine	Urine	160	146	91.3	2.1
		400	439	110	2.0
		640	697	109	2.2
	Serum	160	179	112	2.4
		400	436	109	2.8
		640	676	106	2.8
Sulfameter	Urine	115	119	103	2.4
		346	352	102	2.7
		756	773	102	1.9
	Serum	115	126	110	2.2
		346	382	110	2.3
		756	814	108	2.6
Sulfadimethoxine	Urine	334	339	101	2.3
		901	929	103	2.7
		1168	1186	102	2.4
	Serum	334	371	111	1.6
		901	933	104	2.1
		1168	1264	108	2.4

Table 4. Determination of sulfadiazine in injections, real urine, and serum samples

Sample	Content	Added	Found	Recovery (%)	RSD n = 5 (%)	HPLC
Injection (g/5 mL)	0.98	0.50	1.52	104	2.2	0.97
		1.00	1.97	99.0	2.0	
		1.50	2.45	96.9	1.8	
Urine (μg/mL)	35.2	20.0	55.0	99.3	2.5	34.8
		40.0	75.4	101	2.2	
		60.0	94.6	99.0	2.0	
Serum (μg/mL)	22.5	20.0	42.2	98,5	2.4	22.1
		40.0	62.2	99.3	2.2	
		60.0	82.7	100	2.2	

Conclusion

Based on the strong quenching effect of sulfonamides on luminol–$[Ag(HIO_6)_2]^{5-}$ CL reaction, a new FI-CL method was proposed for the determination of sulfonamides. The new method offers several advantages over other methods: is faster, uses simple instrumentation, and the reagents are stable and inexpensive. It is indicated that the proposed method provides the sensitivity and linearity necessary for analysis of any test sulfonamides in pharmaceutical and biological fluids at clinically relevant concentrations.

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