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Usefulness of Ytterbium(III) as Analytical Reagent for Total Sulfite Determination in White Wine Samples

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Ytterbium(III) is used as reagent for the determination of sulfite by measuring the formation of the Yb(III)−sulfite complex through the variation of the light scattering intensity with time. The low solubility of this complex causes an efficient dispersion of the radiation at 490 nm, which is measured at 980 nm. Each kinetic datum is automatically obtained in only 0.5 s by stopped-flow mixing technique. The application of the initial rate method using a long emission wavelength minimizes the potential interference of fluorescent background signals from the sample matrix. The dynamic range of the calibration graph is 1−250 μg/mL, and the calculated detection limit is 0.35 μg/mL. The precision, expressed as relative standard deviation, is <6%. The method has been applied to the determination of total sulfites in white wine samples, which requires only the sample dilution and the use of two aliquots to improve selectivity. However, the matrix effect found for red wines precludes the application of the method to the direct analysis of these samples. Analytical recoveries ranged from 96.0 to 106.7%. The results obtained with the proposed method agreed with those provided by the *p*-rosaniline method. Unlike this method, in which toxic reagents are required, the use of ytterbium(III) as analytical reagent shows the advantage of its low acute toxic rating.

KEYWORDS: Ytterbium; long-wavelength measurements; total sulfite; white wine samples

INTRODUCTION

Trivalent lanthanides have attracted interest as analytical reagents in recent years owing to the special luminescent properties of some chelates of these ions, which are the result of an efficient intramolecular energy transfer process from the excited triplet state of the ligand to the emitting level of the lanthanide ion. Eu(III) and Tb(III) ions, which emit green and red light, have been extensively used for analytical purposes (*1*, *2*), but other lanthanide ions such as Yb(III), Nd(III), and Er(III), which emit in the near-infrared (NIR) region, have been scarcely described as analytical reagents. The spectral properties of some chelates of these ions with porphyrins (*3*), azo compounds (*4*−*7*), calixarenes (*8*), and macrocyclic compounds (*9*−*12*) have been studied, and an Yb(III) chelate has been described as a label in a qualitative immunoassay method for human chorionic gonadotropin (*13*). The scarce analytical applicability of these ions can be ascribed in part to the fact that the luminescence of their chelates in solution is strongly influenced by some factors such as dissolved oxygen or −OH oscillator vibrations (*5*, *8*).

Sulfites are frequently used as preservatives in the production of dehydrated fruits, fruit juices, syrups, concentrates, or puree and in the course of winemaking (*14*). In the latter case, they can be also present naturally due to some metabolic processes derived from the mineral absorption from soils. The presence of sulfites in the medium prevents the growth of yeast, molds, and bacteria and also the discoloration of carbonyl groups produced by enzymatic and nonenzymatic oxidation reactions. The determination of free and/or total sulfites is common in wine laboratories as these parameters affect the sensory properties and evolution of wines. Total sulfite can be determined using an appropriate alkaline treatment (*15*). A negative aspect of the use of sulfites as food preservatives is that they can cause allergenic responses in asthmatics and skin sensitivity. Also, they interact with some vitamins such as thiamin, pyridoxal, nicotinamide, and folic acid, reducing the nutritional quality of treated foods (*16*).

The traditional method for the determination of sulfites in foods and beverages is the Monier−Williams method (*17*), which involves an acid distillation step to release sulfite as sulfur dioxide, which is transferred, using a carrier gas stream, to an oxidizing trapping solution containing hydrogen peroxide in an alkaline medium. The sulfite content is then determined by titration or gravimetrically as sulfate. The *p*-rosaniline method (*18*) has been also accepted by the AOAC for the determination of sulfites in foods, although the toxicity of the reagents required (formaldehyde, tetrachloromercurate, and *p*-rosaniline) could be a limitation. This method has been applied to the analysis of wine samples using a gas diffusion unit to prevent color interference of red wine (*19*). Other methods for sulfite determination have been described using liquid chromatography

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with UV (*16*), fluorescence (*20*), and conductivity (*15*, *21*) detection and capillary electrophoresis with both UV (*22*) and conductivity (*23*, *24*) detection. In some instances, a previous conversion of sulfites into sulfates using hydrogen peroxide is required to improve selectivity (*15*, *21*). Most of these methods (*15*, *21*−*23*) have been applied to the determination of free or total sulfite in wine.

The present method describes the use of ytterbium as reagent to obtain the initial rate of the Yb(III)−sulfite complex formation, which is used as the analytical parameter. The low solubility of this complex allows measurements of changes in light scattering intensity with time, which are obtained using a spectrofluorometer furnished with a NIR emission monochromator and a sensitive detector to obtain dispersion signals at a long wavelength. This approach can minimize the potential interference of some background signals. The system is developed in aqueous solution, avoiding the presence of organic solvents such as dimethyl sulfoxide or dimethylformamide, which have been used to obtain luminescence signals of several Yb(III) complexes previously reported (*8*). The high initial rate of the Yb(III)−sulfite complex is automatically measured using a stopped-flow mixing technique, which also allows the automatic mixing of the reactants. To the best of our knowledge, there is no previous publication on the use of a lanthanide ion to determine sulfites.

MATERIALS AND METHODS

Apparatus. An SLM Aminco (Urbana, IL) AB2 luminescence spectrometer equipped with a 150 W xenon lamp was used. A 9050 visible and NIR monochromator and an R636-10 Hamamatsu red-sensitive photomultiplier tube, both supplied by ScienceTech (London, ON, Canada), were fitted to the T-format configuration of the instrument to obtain long-wavelength measurements. The instrument was also furnished with a stopped-flow module (*25*). The observation cell of the module has a path length of 1 cm, and the excitation and emission slits were adjusted to provide 4 and 16 nm band-passes. Initial rate measurements were obtained at room temperature.

Reagents. All chemicals used were of analytical reagent grade. A 0.01 g/L stock solution of sodium sulfite (Merck, Darmstadt, Germany) was prepared daily in distilled water. A 0.02 mol/L ytterbium(III) solution was made by dissolving an appropriate amount of ytterbium(III) nitrate pentahydrate (Sigma-Aldrich, Schnelldorf, Germany) in distilled water. A 1 mol/L sodium hydroxide (Merck) solution was used to adjust the pH.

Procedures. *Determination of Sulfite.* An aqueous solution containing Yb(III) (0.02 mol/L, pH 6.7) was used to fill one of the two 2-mL drive syringes of the stopped-flow module. The other syringe was filled with standard or wine sample solution containing from 1 to 250 μg/mL sulfite at pH 9.0. In each run, 0.15 mL of each solution was mixed in the mixing chamber, and the variation of the light scattering signal throughout the reaction was monitored at $\lambda_{ex} = 490$ and $\lambda_{em} = 980$ nm for 2 s. Data were processed by the computer, furnished with a linear regression program for application of the initial-rate method. The reaction rate was determined in ~0.5 s, and each standard or sample was assayed in triplicate. The blank signal was subtracted from each measurement.

Determination of Total Sulfite in White Wine Samples. Two 1-mL aliquots of white wine samples were used. One aliquot was treated with 0.4 mL of 0.5 mol/L sodium hydroxide and mixed by stirring for 30 s. Afterward, the pH of the solution was adjusted to 9.0 and diluted to 10 mL with distilled water. This solution was used to fill one of the drive syringes of the stopped-flow module. A similar procedure was used for the second aliquot, but including also its treatment with hydrogen peroxide (0.2%) for ~2 min to achieve the oxidation of sulfite to sulfate. The signal corresponding to sulfite was calculated by subtracting the signal given by the second aliquot from that obtained by analyzing the first aliquot.

RESULTS AND DISCUSSION

Study of the System. Although the formation of insoluble complexes of lanthanide ions with sulfites has been previously described (*26*, *27*), the potential analytical application of these reactions has not been studied to date. Several assays have been carried out to study the kinetic behavior of Nd(III), Eu(III), Tb(III), and Yb(III) with sulfites by measuring the variation of the light scattering intensity with time using a stopped-flow mixing technique. The best kinetic curves were obtained using Yb(III) at a pH close to the formation of its hydroxide. Electron diffraction analysis by X-ray (EDAX) and IR spectroscopy were used to study the composition of the white precipitate formed. EDAX analysis showed the presence of ytterbium, sulfur, and oxygen in the precipitate. The IR spectrum showed an intense band at 3407 cm^{-1}, which can be ascribed to an −OH stretch and also to the presence of S−O bonds. Also, there were some bands at 631 and 1013 cm^{-1}, which could be attributed to compounds containing bisulfite or sulfite. Taking into account that lanthanide ions are oxidizing agents, Yb(III) could partially convert sulfite into sulfate ions, and the presence of these ions could be explained by a band appearing at 1130 cm^{-1}. Other bands appearing at 1384, 1459, 1520, 1562, and 1643 cm^{-1} can be ascribed to nitrate ions and N−O stretch. As Yb(III) ions were obtained from a nitrate salt, this anion could also be present in the ytterbium coordination sphere, taking into account the high coordination number of lanthanide ions and the high concentration of the ytterbium salt used (2×10^{-2} mol/L) to obtain the precipitate.

The selection of the optimum excitation (λ_{ex}) and emission (λ_{em}) wavelengths was carried out obtaining the light scattering spectrum of the Yb(III)−sulfite system by scanning simultaneously with the same λ_{ex} and λ_{em}. The highest light scattering signal was obtained at 490 nm. Also, this wavelength allowed the maximum initial rate of the system to be obtained. A limitation of this approach is that the presence of a fluorescent species that absorbs or emits at a wavelength close to 490 nm could interfere with this analytical signal. This fact was checked measuring the initial rate of the system in the absence and presence of a 10^{-6} mol/L fluorescein ($\lambda_{ex} = 487$, $\lambda_{em} = 510$ nm) solution, obtaining a decrease in the initial rate of 4 times when fluorescein was present. The same assay was carried out using the second-order grating effect, maintaining the same λ_{ex} but changing the λ_{em} at 980 nm. In this instance, the initial rate of the system decreased by only 10% in the presence of fluorescein, which shows that the selectivity obtained by measuring light scattering intensity can be improved using this long λ_{em}. The instrumentation available, with a xenon lamp, did not allow data to be obtained using the λ_{ex} at 980 nm. Thus, $\lambda_{ex} = 490$ and $\lambda_{em} = 980$ nm were chosen to study the Yb(III)−sulfite system, using the second-order grating effect, which allows the potential interference of blank signals to be minimized.

The method presented here reports a new alternative approach for the use of lanthanide ions as analytical reagents by monitoring the variation of light scattering intensity with time and measuring the initial rate of the system. The use of a stopped-flow mixing technique simplifies the mixing of reagents and allows the automatic acquisition of kinetic data, obtaining each measurement in only 0.5 s. **Figure 1** shows several kinetic curves obtained at different sulfite concentrations, and by using these wavelengths, a linear relationship between the initial rate and sulfite concentration was observed.

Several organic solvents were assayed to study their potential effect on the initial rate of the system. **Table 1** shows the results

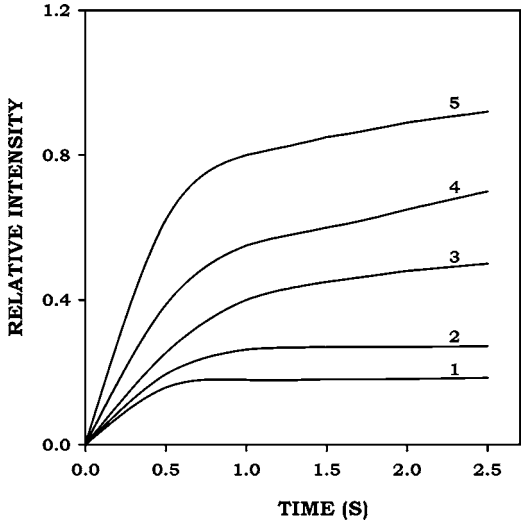

Figure 1. Kinetic curves obtained at $\lambda_{ex} = 490$ and $\lambda_{em} = 980$ nm at different sulfite concentrations: (1) 0; (2) 16; (3) 50; (4) 100; (5) 200 μg/mL. [Yb(III)] = 0.02 mol/L.

Table 1. Influence of Different Solvents and Other Species on the Initial Rate of the System

solvent[a]	initial rate ratio (%)	solvent[a]	initial rate ratio (%)
water	100.0	2-propanol	37.7
ethanol	80.2	acetone	37.7
dimethyl sulfoxide	70.4	methanol	35.4
dimethylformamide	67.3	β-cyclodextrin	7.8
acetonitrile	63.0	polyvinyl alcohol	28.4
ethylene glycol	55.1	gelatin	0.0

[a] The percentage of each solvent was 10% excepting for polivinyl alcohol and β-cyclodextrin which was 0.67%.

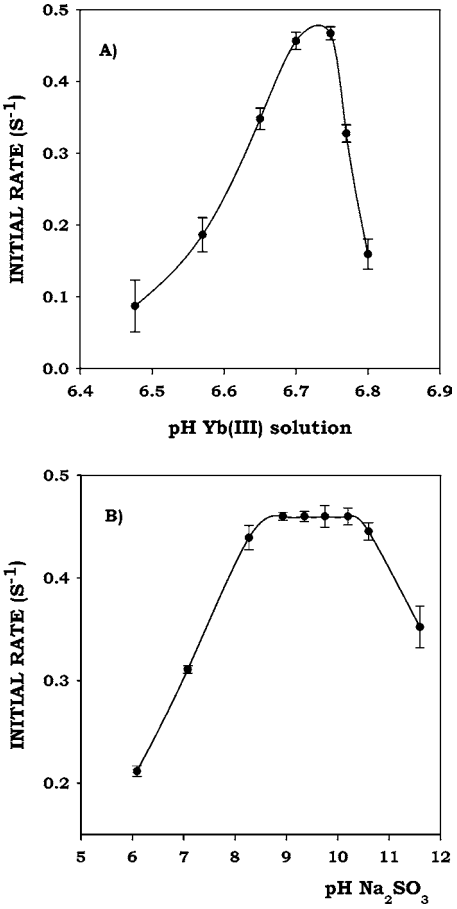

Figure 2. Influence of pH of the ytterbium (**A**) and sulfite (**B**) solutions on the initial rate of the system. [Yb(III)] = 0.02 mol/L; [sulfite] = 100 μg/mL.

obtained and includes also the effect of β-cyclodextrin, polyvinyl alcohol and gelatin, which were assayed to modify the properties of the medium such as viscosity and rigidity. As can be seen, the best initial rate is obtained in aqueous medium. Also, the potential effect of the surfactants cetyltrimethylammonium bromide, sodium dodecyl sulfate, and Triton X-100 was studied at concentrations below and above their critical micellar concentration, but the initial rate of the system did not improve in any case.

Optimization of Variables. The variables affecting the system were optimized by the univariate method. All reported concentrations are initial concentrations in the syringes (twice the actual concentrations in the reaction mixture at time 0 after mixing). Each kinetic result was the average of three measurements. Those values yielding the minimum possible standard deviation for the initial rate, under conditions where the reaction order with respect to the species concerned was 0 or near 0, were taken as optimal.

The pH of the reaction medium is a critical variable that required its separate optimization in both ytterbium and sulfite solutions. Panels **A** and **B** of **Figure 2** show the results obtained, in which it can be seen that the optimum pH range of the ytterbium solution is very narrow and coincides with the pH at which the ytterbium hydroxide starts its formation (*28*). This behavior indicates that the presence of hydroxyl groups is required for the formation of the complex and justifies in part the broad band appearing at 3407 cm^{-1} in the IR spectrum. When the pH of the ytterbium solution was 6.7, the optimum pH range of the sulfite solution was 8.5−10.5 (**Figure 2B**), obtaining a pH range in the reaction medium of 6.5−6.6, as measured in the waste. This decrease in the pH of the mixture could be ascribed to the hydrolysis reaction of the ytterbium excess. Several buffer solutions [hexamethylenetetramine (hexamine), imidazole, and ammonium acetate] were assayed to fit the optimum pH of the ytterbium solution, but a decrease in the initial rate was obtained in all instances. For this reason, the pH was finally adjusted using hydrochloric acid and/or sodium hydroxide solutions. **Figure 3** shows the effect of the ytterbium concentration on the initial rate of the system, in which can be seen that it is independent of this variable in the range 1.8×10^{-2}−2.5×10^{-2} mol/L.

Analytical Features. The kinetic curves obtained under optimum conditions and using $\lambda_{ex} = 490$ and $\lambda_{em} = 980$ nm to monitor the variation of the light scattering intensity with time were processed using initial rate measurements, which were obtained in ~0.5 s. The dynamic range of the calibration graph was 1−250 μg/mL. The difference between the initial rate obtained in the presence and in the absence of sulfite can be linearly correlated with sulfite concentration, the regression equation being $v = (2.2 \pm 2.1) \times 10^{-4} + (4.6 \pm 0.2) \times 10^{-3}X$, where v is the initial rate, expressed in s^{-1}, and X is the sulfite concentration expressed in μg/mL. The Pearson's correlation coefficient (r) is 0.996, which is indicative of a good linearity of the calibration curve. The detection limit calculated following IUPAC recommendations (*29*) was 0.35 μg/mL. Another calibration graph was also obtained using equilibrium measurements, which were measured 10 s after the mixing of the reactants, but the dynamic range (6.4−100 μg/mL) was narrower

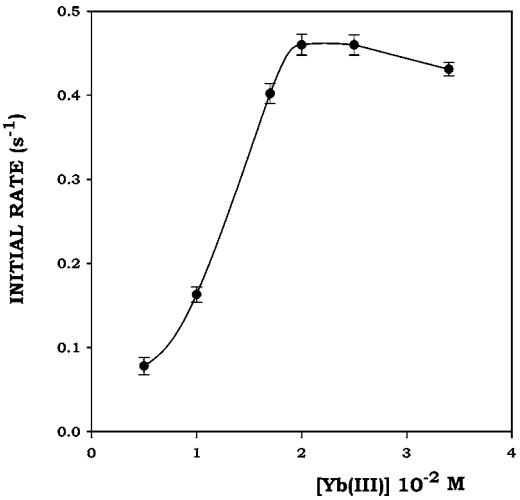

Figure 3. Influence of ytterbium concentration on the initial rate of the system. [sulfite] = 100 μg/mL.

Table 2. Influence of Foreign Substances over the Determination of 10 μg/mL Sulfite

compound	max tolerated interferent/ analyte ratio[a]	compound	max tolerated interferent/ analyte ratio[a]
fructose	500	F^-	100
glucose	500	ascorbic acid	60
Cu^{2+}	100	SO_4^{2-}	20
acetic acid	100	tartaric acid	20
Ca^{2+}	100	succinic acid	10
Fe^{3+}	100	2-mercapto-1-methyl-imidazole	10
K^+	100		
Na^+	100	vanillic acid	10
NO_2^-	100	S^{2-}	10
NO_3^-	100	CO_3^{2-}	5
Cl^-	100	PO_4^{3-}	

[a] Maximum concentration tested was 5000 μg/mL.

and the detection limit (1.9 μg/mL) was higher than those obtained using the kinetic method. Thus, this method was chosen for the determination of sulfites and applied to the analysis of wine samples. As indicated in the procedure for wine analysis, each sample is diluted 10 times, so that the detection limit in the original samples is 3.5 μg/mL, which is similar to the detection limits reported for other sulfite methods (*15*, *23*, *24*).

The precision of the method was assessed at two different sulfite concentrations, 20 and 100 μg/mL, and expressed as the percentage of relative standard deviation, giving 5.8 and 1.2%, respectively. The selectivity was evaluated by assaying some species that can be present in wine samples, which could be considered as potential interferents. A substance was considered not to interfere if the initial rate obtained in the presence of the interferent was within one standard deviation of the signal obtained in its absence. **Table 2** lists the maximum tolerated interferent/analyte ratio, in which it can be seen that only phosphates interfere at the same concentration level as that of the analyte. This interference can be ascribed to the formation of the ytterbium phosphate, which would contribute to the scattering phenomenon in the same way as sulfite ions do. Taking into account that wine samples can contain phosphates and other potential interferents, a calibration graph was obtained by preparing two series of standards and treating one of them with hydrogen peroxide to transform sulfite into sulfate, so that the initial rates obtained for these standards can be taken as the blank signals, as sulfate does not interfere up to a concentration

Table 3. Analysis of White Wine Samples

sample	pH	total titratable acidity (g of tartaric acid/L)	content (μg/mL) *p*-rosaniline method[a]	content (μg/mL) proposed method[a]
1	3.01	3.88	36.7 ± 0.1	33 ± 2
2	3.06	5.02	44.03 ± 0.03	45 ± 4
3	3.04	5.54	327.1 ± 0.2	331 ± 6
4	3.02	5.18	176.46 ± 0.05	185 ± 10
5	2.95	5.54	23.63 ± 0.02	29.36 ± 0.04
6	3.12	4.82	34.26 ± 0.02	33.47 ± 0.03
7	3.08	6.77	113.5 ± 0.1	117.07 ± 0.2
8	3.18	4.77	104.64 ± 0.07	103.96 ± 0.07

[a] Mean ± SD (n = 5).

Table 4. Recoveries of Sulfite Added to White Wine Samples

sample	added (μg/mL)	found[a] (μg/mL)	recovery (%)
1	75	73 ± 2	97.3
	100	102 ± 5	102.0
	150	151 ± 6	100.7
2	75	77 ± 1	102.7
	100	98 ± 2	98.0
	150	160 ± 1	106.7
3	75	77 ± 7	102.7
	100	106 ± 4	106.0
	150	159 ± 10	106.0
4	75	74 ± 1	98.7
	100	99 ± 5	99.0
	150	145 ± 8	96.7
5	75	73.7 ± 0.9	98.3
	100	103 ± 3	103.0
	150	146 ± 9	97.3
6	75	76 ± 2	101.3
	100	100 ± 2	100.0
	150	154 ± 6	102.7
7	75	80 ± 3	106.7
	100	96 ± 6	96.0
	150	160 ± 10	106.7
8	75	75.8 ± 0.8	101.1
	100	99 ± 4	99.0
	150	144 ± 5	96.0

[a] Mean ± SD (n = 5).

20 times higher than that of sulfite. The same equation of the calibration graph as that given above was obtained using the difference between the initial rate measured in the presence and absence of hydrogen peroxide for each standard as the analytical parameter.

Applications. The proposed method was applied to the analysis of several wine samples. The addition of a diluted alkali solution releases the bound sulfite fraction, which allows the determination of total sulfite content analyzing the sample immediately after the treatment. Each sample was treated according to the procedure described above, and the sulfite concentration was calculated by interpolating on the calibration graph. White wine samples were directly analyzed, giving satisfactory results, but the red wine samples assayed gave an excessively high initial rate that precluded their analysis. The application of the proposed method to these samples would require the previous separation of sulfite, in a similar way to other methods such as the Monier−Williams (*17*) and *p*-rosaniline (*18*) methods. **Table 3** shows the results obtained by using the proposed method and those obtained by applying the *p*-rosaniline method, which was used as reference. The table also shows the pH and the total titratable acidity of the analyzed

samples. The application of the paired *t* test (*30*) showed that there were not any significant differences in the results given by both methods. Sulfite was present in all samples assayed, and only one of them contained sulfite in a concentration higher than that allowed by European legislation (*31*), which is as much as 275 μg/mL when the sugar content is $\geq$5 g/L.

An additional advantage of the use of ytterbium as reagent is its very little acute toxicity and noncarcinogenicity if compared with the *p*-rosaniline method, in which the reagents used, *p*-rosaniline, formaldehyde, and tetrachloromercurate, show an acute toxicity and/or potential carcinogenicity. **Table 4** also lists the analytical recoveries obtained by the proposed method, which were calculated by adding three different amounts of sulfite to each sample and subtracting the results obtained from similarly unspiked samples. The recoveries ranged from 96.0 to 106.7%.

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