Sensitive Determination of Sulfate in Drinks and Vegetables Digests by Rayleigh Light Scattering Technique

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In this paper, a novel and sensitive method based on Rayleigh light scattering technique (RLS) was proposed for the determination of sulfate using a conventional spectrofluorometer. Sulfate was transformed to $BaSO_4$ particles, which displayed intense light scattering in aqueous solutions. The effects of factors such as wavelength, acidity, stabilizers and interferents were studied in detail. The RLS intensity of the $BaSO_4$ suspension was obtained in 0.1 mol L^{-1} of $[H^+]$ and the addition of 2 mL of cationic polyacrylamide (CPAM) with 7.05×10^{-3} mmol mL^{-1} charged cations and 1.0 mL of $BaCl_2 \cdot 2H_2O$ (5.0%) at 510 nm. In the range of 8–400 μg mL^{-1}, RLS intensity was linear to the concentration of $BaSO_4$, and the detection limit was 0.3 μg mL^{-1}. To determine the feasibility of the proposed method, some samples of water, drinks, and vegetables digests were analyzed, and the results were in agreement with the standard turbidimetric method. Good recovery results were also obtained in the range of 94–105%. Although this method was limited in stability, it was characterized with simplicity, sensitivity, reliability, and little interference.

KEYWORDS: Sulfate determination; Rayleigh light scattering; barium sulfate

INTRODUCTION

Sulfate is an abundant ion in the earth's crust and high concentrations may be present in water due to leaching of gypsum, sodium sulfate, and some shales (*1*). In natural water, sulfate concentrations range from a few milligrams to several thousand milligrams per liter. Although low amounts of sulfate in water have little adverse effect, when the concentration of sulfate is up to 250 mg L^{-1}, it will affect the taste of water and exert a cathartic action to people for the coexistence of magnesium or sodium ions. Sulfate is also an essential nutrient for plant by exerting important influence on its growing and participating in metabolism to form amino acids and other organic compounds, of which deficiency will affect the crop (*2*). As increasing need for elimination of pollution in water and more basic investigations into the role of the compounds such as amino acids in life processes are conducted, greater demands are placed on sensitive, rapid, precise, and accurate methods for determining sulfate.

There are numerous proposed methods to determine sulfate. The classical gravimetric method is well-known to perform the determination of sulfate accurately (*1*, *3*). Nevertheless, it is traditionally used for the measurement of "percentage-level" concentration, and the process is time-consuming, complex, and inconvenient for large numbers of samples' determinations.

EDTA titrimetric method (*1*), an indirect determination method, requires several reaction hours for sulfate precipitation after the addition of excessive barium ions and it is hindered by the difficulty in judging the end point of titration. Another conventional method, turbidimetry has been used widely for the determination of sulfate in natural waters for a long time. It was also applied to a number of samples' determination through automated flow analysis systems, but all of them are detected by spectrophotometer (*4*–*7*). Therefore, turbidimetry suffers from the disadvantage of low sensitivity and inapplicability to low sulfate containing samples.

In recent years, Rayleigh light scattering (RLS) has been applied to determine a variety of metal ions (*8*–*10*) and biological macromolecules including nucleic acids (*11*–*13*) and proteins (*14*–*20*) in analytical chemistry, owing to its higher sensitivity and better selectivity, which were obtained by the enhancement of RLS intensity (*21*). The RLS bands are expected for aggregation at wavelengths where the molar absorbance of the associate is large. Subsequently, a series of determination methods based on the interaction of protein or nuclei acids and small dyes molecules by RLS technique was established. However, the determination of sulfate by RLS technique has not been reported.

In the present work, a sensitive and simple RLS method was developed to determine sulfate by adding barium to increase the RLS intensity for the formation of the $BaSO_4$ suspension. To prevent the $BaSO_4$ particles from precipitation and agglomeration, CPAM served as the stabilizer. The experiment results

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showed that RLS intensity of the $BaSO_4$ suspensions was linear to the concentration of sulfate so that sulfate can be quantified. The method was applied to the analysis of water and vegetable samples, results of which were consistent with the standard turbidimetric method (*4*), and their recoveries were in the range of 94−105%.

MATERIALS AND METHODS

Apparatus. The RLS spectra were obtained by synchronous scanning on a Shimadzu RF-5301 PC spectrofluorophotometer (Japan) in the wavelength region from 250 to 750 nm. The width of excitation and emission slits was set at 3.0 nm. RLS intensity was measured at 510 nm using a Hitachi M-850 fluoroscence spectrometer (Japan), with a slit width of 5.0 nm for excitation and emission. The adsorption spectrum was recorded with a Cary-50 UV−vis spectrometer (Varian, Palo Alto, CA). An IRIS plasma spectrometer of Thermo Jarrell Ash Corporation was used to determine metal elements in samples.

Reagents. All reagents were of analytical-reagent grade unless otherwise mentioned. All solutions were prepared with Mili-Q water.

A stock solution containing 1000 μg mL^{-1} of sulfate is prepared by dissolving 1.4790 g of dehydrate sodium sulfate in water and diluting to 1000 mL. Working solutions were obtained by diluting the stock solution just prior to use.

Barium Chloride Dihydrate (5.0%) Solution. A 12.50-g sample $BaCl_2$ · $2H_2O$ was dissolved and made up to 250 mL. If a slight amount of precipitate developed, the solution must be filtered before used.

Cationic Polyacrylamide (CPAM) (5.0%, w/w). Polyacrylamide was hydrolyzed to carry 50% charged cations and then diluted directly with water. The concentration of charged cations was 7.05×10^{-3} mmol mL^{-1}.

Samples. The samples of table water, mineral water, and pure water were filtered if there was some precipitate. Vegetables and drinks were prepared by wet-digestion procedures. The samples of vegetables were washed, and 25.00 g of each sample was weighed and predigested with 10 mL of concentrated nitric acid at a temperature not exceeding 160 °C, and then excessive nitric acid was driven away by addition of 2.0 mL of perchloric acids. Heating was continued until a clear, colorless solution was obtained and dense fumes appeared. After the solution was cooled, the digests were diluted to a specified volume of 50.00 mL.

A 20.00-mL aliquot of each drink was placed in a 100-mL Pyrex beaker and heated gently until carbon dioxide was removed completely. The following treating steps were the same as those of the vegetables.

A 3.0-mL aliquot of 100 μg mL^{-1} SO_4^{2-}, 1.0 mL of 1M HCl, and 2.0 mL of 5.0% CPAM were mixed in a 10.0-mL colorimetric tube. Then, the mixture was diluted to 8 mL and vertexed. After 1.0 mL of $BaCl_2$ · $2H_2O$ (5.0%) was added dropwise, the mixture was diluted to 10 mL and blended thoroughly. RLS intensity was measured with a 10-mm quartz cell at the wavelength of 510 nm for excitation and emission after the placement for 10 minutes.

Sulfate in each sample was determined by a method similar to the procedures mentioned above. A 1- or 3-mL aliquot of the prepared sample solutions was added to the colorimetric tube instead of 3.0 mL of 100 μg mL^{-1} SO_4^{2-}.

RESULTS AND DISCUSSION

Light Scattering Spectra. Figure 1 shows RLS spectra of the blank solution without SO_4^{2-} (curve1) and the $BaSO_4$ suspension (curve 2). RLS intensity of the blank solution (curve 1) was weak over the whole scanning region. However, when a little SO_4^{2-} was added in the aqueous medium, RLS intensity was greatly enhanced in the wide range of 300−600 nm, which sufficiently indicated that a new species of barium sulfate had been formed through electrostatic action. According to the spectra, a random wavelength from 340 to 550 nm can be selected for the determination. Because the RLS intensity at λ = 510 nm was the maximum and adsorption was little at this
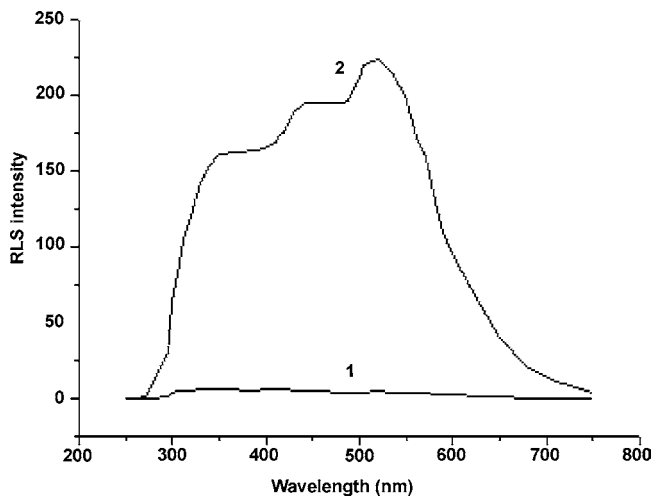

Figure 1. RLS spectra of two solutions: (1) the blank solution, (2) the $BaSO_4$ suspension. Conditions: 30 μg mL^{-1} of $[SO_4^{2-}]$, 0.1 mol L^{-1} of $[H^+]$, 2.0 mL of CPAM with 7.05×10^{-3} mmol L^{-1} charged cations, and 1.0 mL of $BaCl_2$ · $2H_2O$ (5.0%) solution were added. The spectra were obtained after placing the solution for 10 min.
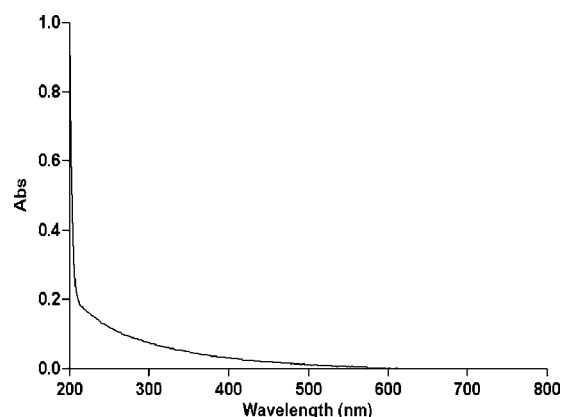

Figure 2. Adsorption spectrum of the $BaSO_4$ suspension.

wavelength as shown in **Figure 2**, in this paper, 510 nm was recommended in view of the sensitivity of the determination.

Light scattering is caused by the presence of fine particles. Because the dimension of $BaSO_4$ particles is much less than the incident wavelength, it should be in accordance with the Rayleigh light scattering formula, which is shown as follows (*20, 22*):

$$R(\theta) = \frac{9\pi^2}{2\lambda^4}\left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2}\right)^2 N_0 v^2 (1 + \cos^2\theta) \qquad (1)$$

where $R(\theta)$ is the Rayleigh light ratio at the scattering angle θ, which is equal to the ratio of the scattering intensity of incident light $I(\theta)$ at the angle θ to the intensity of incident light I_0; n_1 and n_0 are the refractive indices of solute and medium, respectively; N_0 is the number of particles per unit volume; v is the volume of the particle; and λ is the wavelength of incident light in the medium.

If c is the concentration of $BaSO_4$ solution, and ρ is the density of each particle, so $N_0 v$ is equal to c/ρ. The formula above can be expressed in eq 2

$$R(\theta) = \frac{9\pi^2}{2\lambda^4}\left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2}\right)^2 \frac{c}{\rho} v (1 + \cos^2\theta) \qquad (2)$$
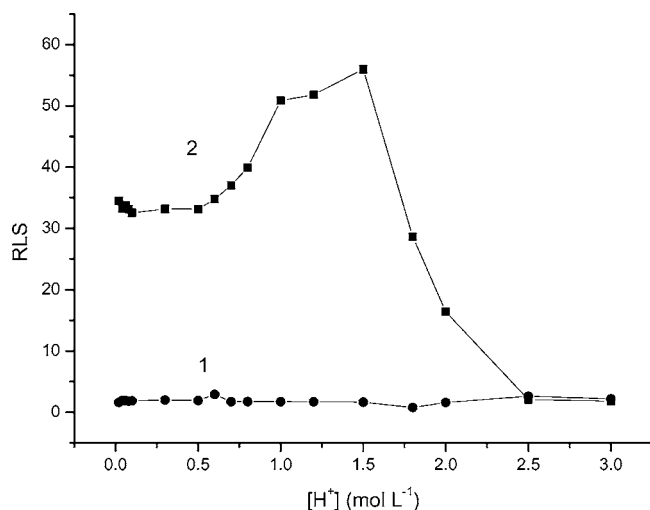
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Figure 3. Effect of [H+] on the RLS intensity: (1) the blank solution, (2) the BaSO4 suspension. Conditions: 30 μg mL^{-1} of [SO$_4^{2-}$], 2.0 mL of CPAM with 7.05×10^{-3} mmol mL^{-1} charged cations, and 1.0 mL of BaCl$_2$ · 2H$_2$O (5.0%) solution were added. The wavelength was set at 510 nm. All data were obtained after placing the solution for 10 min.

Figure 4. Effects of different stabilizers on RLS intensity as a function of time. The legend symbols represent different added stabilizers: A, none; B, CPAM; C, ethanol; D, glycerol; E, (2:1) ethanol to glycerol; F, (1:1) ethanol to glycerol; G, (1:2) ethanol to glycerol. Conditions: 30 μg mL^{-1} of [SO$_4^{2-}$], 0.1 mol L^{-1} of [H+], 2.0 mL of each stabilizer, and 1.0 mL of BaCl$_2$ · 2H$_2$O (5.0%) solution were added. The wavelength was set at 510 nm.

In the experiment, θ is 90°, υ remained nearly constant because the experiment conditions such as acidity and the adding volume of stabilizer and other reagents were kept as identical as possible to obtain the same size particles; n_1, n_0, λ and ρ were all constant. According to eq 2, RLS intensity is proportional to the concentration of BaSO4 suspension (c) or the number of particles in the unit volume (N_0). Therefore, sulfate can be determined based on this theory.

Effect of Acidity. The effect of acidity was studied in the H+ concentration range of 0–3 mol L^{-1} (**Figure 3**). As shown from **Figure 3**, acidity had significant effects on RLS intensity. RLS intensity decreased after the addition of a little HCl and kept stable in the H+ concentration range of 0.04–0.6 mol L^{-1}. When more HCl was added, the RLS intensity increased, and the highest RLS intensity was obtained at 1.5 mol L^{-1} of [H+]. Larger than 1.5 mol L^{-1} of [H+], RLS intensity decreased dramatically.

The effects of acidity can be interpreted as follows: Without the addition of HCl, coexisting ions such as CO$_3^{2-}$, SO$_3^{2-}$, PO$_4^{3-}$, etc. would affect the RLS intensity by their combination with Ba^{2+}. When a little HCl was added, their interference could be eliminated. The increase of RLS intensity at [H+] higher than 0.6 mol L^{-1} was caused by the increase of ionic strength when excessive HCl was added, because strong ionic strength would result in smaller sizes of particles and the increase of particle numbers. However, soluble H$_2$SO$_4$ and HSO$_4^-$ complexes were formed at [H+] higher than 1.5 mol L^{-1}. The reaction competed with the formation of BaSO4 particles, so RLS intensity decreased dramatically. Because RLS intensity was stable in the [H+] range of 0.04–0.6 mol L^{-1}, [H+] was kept at 0.1 mol L^{-1} in this experiment.

Effect of Stabilizer. The formation process of BaSO4 particles includes three steps (*23*): nucleation, crystal growth, and aggregation, which will affect the sizes of the particles directly. Because the size of the particles is one important factor deciding RLS intensity, stabilizer must be used to control the size of barium sulfate particles, prevent the rapid sedimentation of the particles, and improve the reproducibility of RLS intensities of solutions that have the same amount of sulfate.

In this paper, some commonly used stabilizers besides ethanol, glycol, and their mixtures were tested. CPAM with
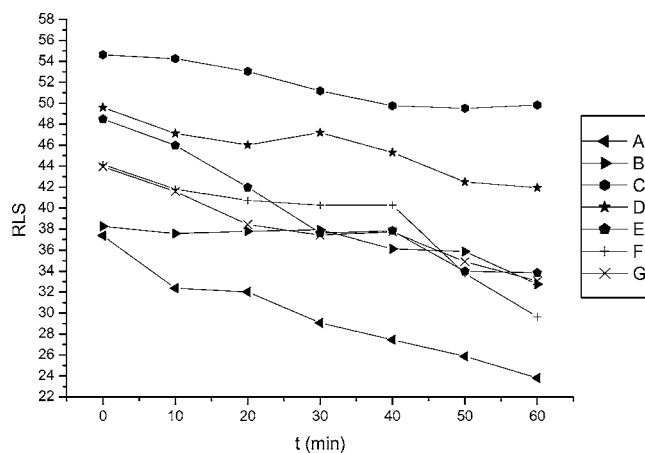
7.05×10^{-3} mmol mL^{-1} charged cations, a cationic polymer, was also applied to stablize the BaSO4 suspension. The stability of each solution was tested by comparing the change of RLS intensity as the function of time with the BaSO4 suspension without the addition of stablilizer. Results were shown in **Figure 4**. Due to the characteristics of barium sulfate particles, RLS intensity of all suspensions decreased gradually in an hour due to precipitation. The suspension with the greatest change of RLS intensity during an hour was that without any stabilizer, and it even changed a great deal in 10 minutes. When a kind of stabilizer was added, the stability of the suspension was increased, and RLS intensity was also increased due to changes of the size of BaSO4 particles.

As shown in **Figure 4**, CPAM has the best ability to stabilize the suspension in half an hour. This was caused by a different mechanism of stabilization. Both ethanol and glycol (*24*) have hydrophilic and hydrophobic groups, so they act as dispersants to prevent the aggregation of BaSO4 particles. However, CPAM with 7.05×10^{-3} mmol mL^{-1} charged cations acts as a stabilizer not only by steric effect but by electrostatic repulsion forces, because it carries positive charges in addition to the hydrophilic and hydrophobic groups (*25*). According to the studies, CPAM has the best stabilizing capacity in half an hour, so CPAM was used as the stabilizer, and the determination must be carried out within half an hour. In this paper, all determinations were carried out after placing the suspensions for 10 minutes.

The effect of the volume of CPAM on the stability was also investigated by adding 1–4 mL of CPAM to make it more effective. It was found that 2 mL of CPAM can stabilize the solution most effectively, so 2 mL of CPAM with 7.05×10^{-3} mmol mL^{-1} charged cations were added into the solution.

Effect of Interferents. Some cationic and anionic species normally found in water and vegetables were studied by the addition of foreign substances. Their concentration relative to [SO$_4^{2-}$] and the corresponding influence to the determinations are displayed in **Table 1**. In the studied species, SO$_3^{2-}$ was affected seriously due to the formation of BaSO3 precipitate. However, SO$_3^{2-}$ was unstable and nearly absent in the sample, so it would not interfere with the determination. The most abundant Na+ would interfere at the concentration of up to 60 times that of [SO$_4^{2-}$]. Because Na+ was studied by adding NaCl

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Table 1. Effect of Interfering Ions on the Sulfate Determination[a]

foreign ion	ratio of the concn (foreign ions/[SO_4^{2-}])	change in RLS (%)	foreign ion	ratio of the concn (foreign ions/[SO_4^{2-}])	change in RLS (%)
Ca^{2+}	10	2.70	CO_3^{2-}	1	2.67
Mg^{2+}	10	−3.65	SO_3^{2-}	1	2.23
Na^+	60	7.6	NO_3^-	10	3.46
Cu^{2+}	1	0.20	NO_2^-	10	0.68
NH_4^+	10	5.54	PO_4^{3-}	10	1.01
Fe^{3+}	1	−3.30	Br^-	10	−0.81
K^+	10	0 0.59	Pb^{2+}	1	7.37
Zn^{2+}	10	6.04			

[a] [SO_4^{2-}] was 30 μg · mL^{-1}, the cationic ions were added in the form of chloride, and the anionic ions were added in the form of sodium.
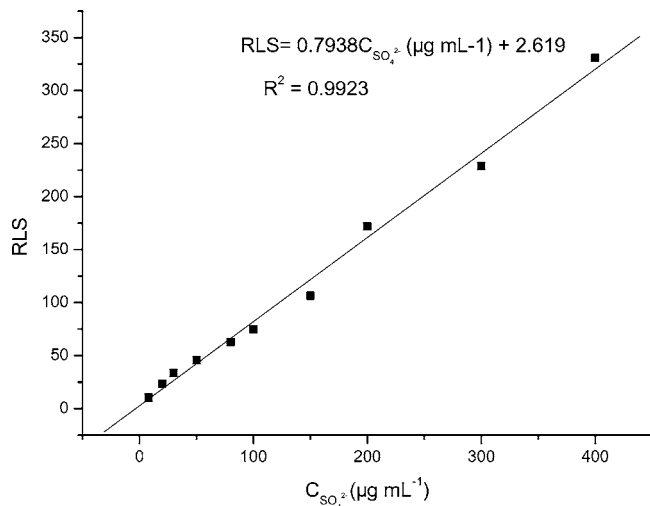

Figure 5. The calibration curve for the determination of [SO_4^{2-}] by RLS technique. Conditions: 0.1 mol L^{-1} of [H$^+$], 2.0 mL of CPAM with 7.05 × 10^{-3} mmol mL^{-1} charged cations, and 1.0 mL of BaCl$_2$ · 2H$_2$O (5.0%) solution were added. The wavelength was set at 510 nm. All data were obtained after placing the solution for 10 min.

and Cl$^-$ had more molecular weight than Na$^+$, the tolerant level of [Cl$^-$] was larger. Other studied ions have nearly no effects on the determination when their concentration was the same or more than [SO_4^{2-}]. Therefore, the tolerant level of interference in the samples was very high. Due to the good selectivity of this method, assays can be performed without removing other coexisting ions.

Calibration Curve and Determination of Ions In Samples. The calibration curve was obtained under optimum conditions (**Figure 5**). The linear regression equation was $I = 2.619 + 0.7938C_{SO_4^{2-}}$ (μg mL^{-1}) ($r^2 = 0.9923$) in the range of 8−400 μg mL^{-1}. The determination limit (*26*) was 0.3 μg mL^{-1}, indicating sensitivity of this method for the determination of SO_4^{2-}. The method was applied to the determination of SO_4^{2-} in a series of samples. The contents of common metallic elements in water and the digests of the drinks and vegetable samples were obtained by induced coupled plasma (**Table 2**), which showed that the concentrations of common cations were within allowed concentration levels and that determination can be performed without pretreatment. **Table 3** lists the consistent results of the determination of SO_4^{2-} by RLS technique and by the standard turbidimetric method (*4*). Recoveries of some samples were also obtained by adding 1 mL of work solution into the samples (**Table 4**). As can be seen in **Table 3** and **Table 4**, RLS method is a reliable, sensitive, and simple method for the determination of sulfate.

Table 2. Content of Common Cations in Waters, Drinks, and Vegetables Digests[a]

cations samples	Al^{3+} (ppm)	Ca^{2+} (ppm)	Cu^{2+} (ppm)	Fe^{3+} (ppm)	Mg^{2+} (ppm)	Pb^{2+} (ppm)	Zn^{2+} (ppm)	Na^+ (ppm)
tape water	0.02	50.91	0.008	0.06	16.92	0.01	0.02	31
mineral water	0.02	8.57	0.002		1.26	0.01	0.02	2
pure water	0.03	5.57		0.002	2.16	0.01	0.007	9
green tea	3.05	20.09	0.76	2.04	4.68	0.12	3.94	119
cabbage	25.62	567.40	0.9	17.92	94.16	0.06	4.3	
cola	2.14	19.35	0.44	2.12	5.42	0.18	0.82	
cucumber	3.99	220.8	1.28	3.96	39.85	0.11	4.03	
spinach	13.45	419.1	0.63	12.27	78.23	0.06	3.21	
carrot	2.03	42.63	0.3	1.99	12.65	0.04	0.88	
tomato	11.46	65.28	0.22	5.56	53.69	0.04	0.94	
tea leaf	17.41	162.4	2.1	13.59	73.6	0.12	3.13	55

[a] No reading indicates not found.

Table 3. Determination Results of Sulfate in Waters, Drinks, and Vegetables Digests[a]

	sulfate			
	RLS technique ($n = 6$)	RSD (%)	turbidimetric method ($n = 6$)	RSD (%)
samples				
tape water	56.93	1.6	54.38	1.8
mineral water	1.85	2.2	1.62	1.5
pure water				
green tea	78.95	0.9	82.20	1.3
cola	57.35	1.2	58.14	1.7
cabbage	865.3	0.4	877.3	1.9
spinach	790.5	0.6	783.5	2.1
carrot	239.5	0.9	230.5	2.6
cucumber	189.5	0.3	196.2	2.5
tomato	125.6	0.8	123.5	1.8
tea-leaf	7720	0.1	7726	2.0

[a] The concentration of SO_4^{2-} in water and drinks samples is expressed in μg mL^{-1} and μg g^{-1} for vegetables samples. No reading is not found.

Table 4. Recovery Tests of Some Samples[a]

sample	sulfate in samples (μg)	added sulfate (μg)	found (μg)	recovery range	R. S. D. (%) ($n = 5$)
tape water	170.8	100	260.3–275.6	96.13%–101.8%	3.2%
mineral water	5.45	100	99.36–101.6	94.22%–96.35%	1.3%
pure water	0	100	93.53–97.86	93.53%–97.86%	2.6%
green tea	94.74	100	191.6–204.3	98.40%–104.9%	3.3%
cola	68.82	100	160.4–177.1	95.00%–104.9%	4.8%
carrot	119.7	100	213.9–220.8	97.37%–100.5%	1.9%
cucumber	94.75	100	185.9–183.4	95.44%–99.30%	2.3%
tomato	62.8	100	159.2–170.1	97.78%–104.5%	3.6%

[a] 1 or 3 mL of samples was used, and 1 mL of the work solution was added to each sample.

RLS technique is useful and sensitive for trace analysis. The present study was undertaken to develop a novel method for the determination of sulfate by RLS technique. In 0.1 mol L^{-1} of [H$^+$] and the addition of CPAM with 1.41 × 10^{-2} mmol charged cations and BaCl$_2$ solutions, sulfate was determined based on RLS technique and the formation of BaSO$_4$. There are linear relationships between the RLS intensity and the concentrations of sulfate in the range of 8−400 μg mL^{-1}, and the detection limit was 0.3 μg mL^{-1}.

Compared with other reported methods for sulfate determination, several differences are obvious. First, the more sensitive RLS technique was applied to determine sulfate by using a conventional spectrofluorometer. Second, the RLS intensity was

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enhanced by the formation of BaSO$_4$ particles. Third, the results show that this method was sensitive and low detection limit was obtained.

To study the feasibility of this study, this method was applied to the determination of sulfate in some samples of water, drinks, and vegetables digests. Their results were consistent with the standard turbidimetric method. Therefore, the determination of sulfate based on RLS technique and the formation of BaSO$_4$ suspensions is practical, sensitive, and reliable.

ABBREVIATION USED

RLS, Rayleigh light scattering; CPAM, cationic polyacrylamide; ICP, inductively coupled plasma atomic emission spectrometry.

LITERATURE CITED

(1) Maděra, V.; Allen, H. E.; Minear, R. A. Nonmetallic constituents. Examination of Water for Pollution Control, 1st ed.; Suess, M. J., Ed.; World Health Organization Regional Office for Europe and Pergamon Press Ltd.: Exeter, Great Britain, 1982; Vol. 2, pp 331−334.

(2) Beaton, J. D.; Burns, G. R.; Platou, J. Determination of Sulfur in Soil and Plant Materials. Sulfur Institute, London. *Tech. Bull.* **1968**, *14*, 1−56.

(3) Thomas, W. V.; Kenneth, W. P.; Gregory, C. T.; Charles, M. B.; Therese, A. B. Using Instrumental Techniques to Increase the Accuracy of the Gravimetric Determination of Sulphate. *Analyst* **1995**, *120*, 2025−2032.

(4) Amarican Society for Testing and Materials. ASTM D516−82. Standard Test Methods for Sulfate Ion in Water. Annual Book of ASTM Standards. American Society for Testing and Materials: Easton, MD. 1983; Vol. 11.01, pp 644−650.

(5) Basson, W. D.; Böhmer, R. G. An Automated Procedure for the Determination of Sulfur in Plant Tissue. *Analyst* **1972**, *97*, 266−270.

(6) Krug, F. J.; Filo, H. B.; Zagatto, E. A. G.; Jørgensen, S. S. Rapid Determination of Sulphate in Natural Waters and Plant Digests by Continuous Flow Injection Turbidimetry. *Analyst* **1977**, *102*, 503−508.

(7) Ricardo Erthal Santelli; Paulo Roberto Salgado Lopes; Regina Célia Leme Santelli; Angela De Luca Rebello Wagener. Turbidimetric Determination of Sulphate in Waters Employing Flow Injection and Lead Sulphate Formation. *Anal. Chim. Acta* **1995**, *300*, 149−153.

(8) Cao, Q. E.; Zhao, Y. K.; Yao, X. J.; Hu, Z. D.; Xu, Q. H. The Application of the Resonance Enchanced Rayleigh Light Scattering Technique For the Determination of Gold (III) with a New Trianzene Reagent. *Anal. Lett.* **2001**, *34*, 773−784.

(9) Liu, S. P.; Liu, Q.; Liu, Z. F.; Li, M.; Huang, C. Z. Resonance Rayleigh Scattering of Chromium (VI)-Iodide-Basic Triphenylmethane Dye Systems and Their Analytical Application. *Anal. Chim. Acta* **1999**, *379*, 53−61.

(10) Liu, S. P.; Liu, Z. F.; Zhou, G. M. Resonance Rayleigh Scattering for the Determination of Trace Amounts of Mercury (II) with Thiocyanate and Basic Triphenylmethane Dyes. *Anal. Lett.* **1998**, *31*, 1247−1259.

(11) Zhang, W. J.; Xu, H. P.; Xue, C. X.; Chen, X. G.; Hu, Z. D. Resonace Light Scattering for the Determination of Nucleic Acids with Methyl Violet. *Anal. Lett.* **2001**, *34*, 553−568.

(12) Zhang, W. J.; Xu, H. P.; Wu, S. Q.; Chen, X. G.; Hu, Z. D. Determination of Nucleic Acids with Crystal Violet by a Resonance Light-Scattering Technique. *Analyst* **2001**, *126*, 513−517.

(13) Huang, C. Z.; Li, K. A.; Tong, S. Y. Determination of Nucleic Acids by a Resonance Light-Scattering Technique with α,β,γ-Tetrakis [4-(trimethylammoniumyl)phenyl]porphine. *Anal. Chem.* **1996**, *68*, 2259−2263.

(14) Guo, Z. X.; Li, L.; Shen, H. X.; Cong, X. Bromopyrogallol Red Enhanced Resonance Light-Scattering Spectroscopic Determination of DNA with 5,10, 15, 20-Tetrakis [4-(trimethylammoniumyl)phenyl]porphine. *Anal. Chim. Acta* **1999**, *379*, 45−51.

(15) Li, Q. F.; Dong, L. J.; Jia, R. P.; Chen, X. G.; Hu, Z. D. Rayleigh Light Scattering Enhanced Reaction of Dibromochloroarsenazo and Proteins System and its Analyticle Application. *Spectrosc. Lett.* **2001**, *34*, 407−417.

(16) Jia, R. P.; Dong, L. J.; Li, Q. F.; Chen, X. G.; Hu, Z. D.; Nagaosa, Y. Study of the Interaction of Protein and Dibromomethyl-Arsenazo-Al(III) by Rayleigh Light-Scattering Technique. *Anal. Chim. Acta* **2001**, *442*, 249−256.

(17) Li, Q. F.; Liu, S. H.; Zhang, H. Y.; Chen, X. G.; Hu, Z. D. Microdetermination of Proteins by Enhanced Resonance Light Scattering Spectroscopy of M-acetylchlorophosphonazo. *Anal. Lett.* **2001**, *34*, 1133−1142.

(18) Guo, Z. X.; Shen, H. X. Sensitive and Simple Determination of Protein by Resonance Rayleigh Scattering with 4-azochromotropic Acid Phenylfluorone. *Anal. Chim. Acta* **2000**, *408*, 177−182.

(19) Dong, L. J.; Jia, R. P.; Li, Q. F.; Chen, X. G.; Hu, Z. D. Study of the Reaction of Proteins with Beryllon II-Al^{III} by the Rayleigh Light Scattering Technique and its Application. *Analyst* **2001**, *126*, 707−711.

(20) Zhang, S. Z.; Zhao, F. L.; Li, K. A.; Tong, S. Y. Determination of Glycogen by Rayleigh Light Scattering. *Anal. Chim. Acta* **2001**, *431*, 133−139.

(21) Yao, G.; Li, K. A.; Tong, S. Y. Study on the Interaction of Protein with Sulfonazo III by Rayleigh Light Scattering Technique and Its Application. *Anal. Chim. Acta* **1999**, *398*, 319−327.

(22) George, A. M. Fluctuation Theory of the Resonance Enhanced of Rayleigh Scattering in Absorbing Media. *J. Phys. Chem.* **1978**, *82*, 616−618.

(23) Smith, C. F.; Nolan III, T. J.; Crenshaw, P. L. Removal and Inhibition of Cacium Sulfate Scale in Waterflood Projects. *J. Pet. Technol.* **1968**, *11*, 1249−1256.

(24) Hough, D. B.; Thompson, L. Nonionic Surfactants. Physical Chemistry. Surfactant Science Series 23; M. J. Schick, Ed.; Marcel Dekker: New York, 1987; pp 601−610.

(25) Michaels, A. S. Aggregation of Suspensions by Polyelectrolytes. *Ind. Eng. Chem.* **1954**, *46*, 1485−1490.

(26) Li, Q. F.; Chen, X. G.; Zhang, H. Y.; Xue, C. X.; Liu, S. H.; Hu, Z. D. The High-Sensitivity Determination of Protein Concentrations by the Enhancement of Rayleigh Light Scattering of Arsenazo-DBN. *Analyst* **2000**, *125*, 1483−1486.