

Research Article

Rapid and Sensitive Determination of Trace Chloride Ion in Drinks Using Resonance Light Scattering Technique

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A resonance light scattering (RLS) technique to determine chloride ions in drinks was developed. Chloride ions were found to bind Ag^+ forming AgCl aggregates that produced intense resonance scattering light. Effects of factors such as acidity, ionic strength, and coexistent interferents on the RLS of AgCl aggregates were investigated. The pH of solution almost did not affect the production of RLS and few foreign species interfered with the detection of chloride ions. The resonance scattering light intensity at the maximum peak of 571 nm was linear to the concentration of chloride ions in the range of 1.42–8.52 ng mL^{-1} with a detection limit of 0.71 ng mL^{-1} . To determine the feasibility of the proposed method, some samples of water and drinks were analyzed. The attained results were in agreement with that of ion-selective electrode method. Good recovery results were also obtained with the range of 94.08–105.63%. The sensitivity and selectivity of the RLS method are high enough to determine trace amounts of chloride ions without any significant interference from high concentration of other components such as common anions and cations.

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1. INTRODUCTION

Resonance light scattering (RLS) is an elastic scattering and occurs when an incident beam in energy is close to an absorption band. Pasternack et al. first established the RLS technique to study the biological macromolecules by means of an ordinary fluorescence spectrometer [1]. Due to its high sensitivity, selectivity, and convenience, RLS studies have attracted great interest among researchers. In recent years, RLS technique has been used to determine pharmaceutical [2–5], ion [6], bacteria [7], and various biological macromolecules, such as nucleic acids [8–10], proteins [11–15], and peptide [16].

Over the years, numerous analytical methods for Cl^- in a variety of samples have been developed, such as ion chromatography [17, 18], near-infrared spectrometry [19], spectroscopy [20], ion-selective electrode method [21], turbidimetric method [22], and so on. Among these methods, the turbidimetric method was popular and regarded relatively reliable for the quantification of Cl^- . Although it often provided very accurate results, it suffered from the long experimental time, lower sensitivity, and complexity. Partly,

because of the lower sensitivity, few of the above methods were applied to determine Cl^- in biological systems. The classical ion-selective electrode method is currently used in food analysis of Cl^- in drinks. Nevertheless, these methods similarly suffered from the drawbacks of low sensitivity and inapplicability to low chloride-containing samples.

The objectives of this report are to establish a rapid, sensitive, and selective RLS analytical method to determine of Cl^- and to develop an alternative standard method for determination of Cl^- in marketing drink. The obtained results were compared with that of the ion-selective electrode method.

2. EXPERIMENTAL

2.1. Apparatus

RLS spectra were recorded on a JASCO FP-6500 spectrofluorophotometer equipped with a thermostated cell compartment using quartz cuvettes (1.0 cm) (Japan). The width of excitation and emission slits was set at 3.0 nm. A Bayer Rapidchem 744 electrolyte analyzer (UK) was used in

the ion-selective electrode detection. The pH measurements were carried out on a PHS-3C Exact Digital pH meter equipped with Phonix Ag-AgCl reference electrode (Cole-Parmer Instrument Co., Ill, USA), which was calibrated with standard pH buffer solutions.

2.2. Reagents

A stock solution containing $355.00 \text{ ng mL}^{-1}$ of Cl^- was prepared by dissolving 0.5850 g of NaCl (>99.99%, Sigma Co., Mo, USA) in doubly distilled water and diluting to 1000 mL . The working solutions were obtained by diluting the stock solution prior to use. A working solution of silver nitrate ($169.87 \mu\text{g mL}^{-1}$) was prepared with doubly distilled water. All other reagents and solvents were of analytical reagent grade and used as purchased. Double-distilled water was used throughout. HAc and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (0.01 mol L^{-1}) were used to control the acidity, while 0.10 mol L^{-1} NaNO_3 was used to adjust the ionic strength of the aqueous solutions.

2.3. Standard procedure

An appropriate aliquot of Cl^- working solution was added to 1.0 mL of silver nitrate working solution and diluted to 10.0 mL with water. After standing for five minutes, the solution was synchronous scanned on the spectrofluorometer through the wavelength range of $250\text{--}750 \text{ nm}$. The obtained RLS spectra were recorded, and the intensity was measured at 571 nm . The enhanced RLS signal of AgCl system was represented as $\Delta I = I - I_0$ (I and I_0 are the RLS intensity of the system in the presence and absence of Cl^- , resp.). The operations were carried out at 20°C .

2.4. Sample

The mineral water, pure water, and green tea commonly found in the supermarket were used as samples. The famous brands such as Nongfu spring, Laoshan, Nestlé, Robust, Watsons, and Masterkong were taken into account. These samples were diluted with double-distilled water and sterilized by filtration ($0.2 \mu\text{m}$) before testing. Chloride ion in each sample was determined by the above-mentioned procedures by adding a 1.0 mL aliquot of the prepared sample instead of the chloride ion working solution.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the RLS spectra

The RLS spectra of Cl^- and AgNO_3 in water were shown in Figure 1(a) and (b), respectively. It can be seen that the RLS intensity of AgNO_3 solution is quite weak in the whole scanning wavelength region. In contrast, upon addition of trace amount of Cl^- to AgNO_3 solution, a remarkably enhanced RLS with a maximum peak at 571 nm was observed under the same conditions (1.0 mL of silver nitrate). The addition of increasing Cl^- to the solution leads to the gradual enhancement in RLS intensity, exhibiting

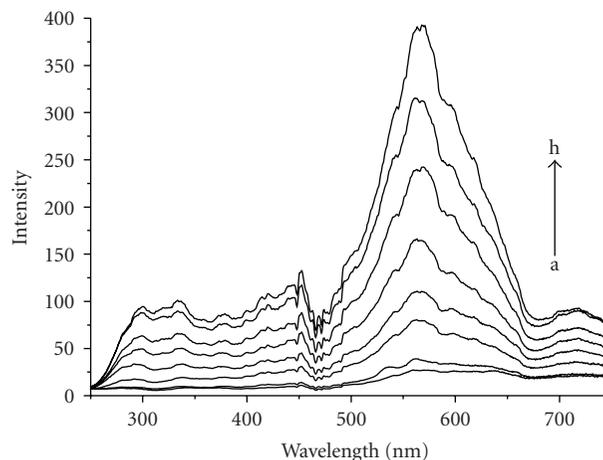


FIGURE 1: RLS profile of AgCl systems. (b)–(h) $6.99 \mu\text{g mL}^{-1}$ of AgNO_3 , 1.0 mg mL^{-1} tween-80, and $0.0, 1.42, 2.84, 4.26, 5.68, 7.10, 8.52 \text{ ng mL}^{-1}$ of Cl^- . (a) 35.5 ng mL^{-1} of Cl^- and 1.0 mg mL^{-1} tween-80.

a concentration-dependent relationship. The production of RLS and its intensity are correlative with the formation of the aggregate and its particle dimension in solution. Bearing on this point, we inferred that the Cl^- ion may displace NO_3^- ion in AgNO_3 (aq), forming a new AgCl (s) compound that could be expected to be an aggregate. The size of AgCl (s) particles may be much less than the incident wavelength, and thus the enhanced light-scattering signal occurs under the given conditions. In this way, the resonance light scattering formula could be applicable to the AgCl system.

3.2. Effects of pH value and ionic strength on RLS

The newly-formed AgCl (s) particles may be ascribed to the higher electrostatic attraction between Ag^+ and Cl^- than that of the coexistent NO_3^- ion. Moreover, the RLS is relevant to the size of the formed aggregated species. Hence, the pH value and ionic strength may exert certain influence on the attraction strength and the dimension of suspension particles, and thus the RLS production and its intensity. The RLS intensity of AgCl and AgNO_3 solution did not change with the variation of pH in range of $2.0\text{--}11.0$. Sodium nitrate was used to maintain the ionic strength of the solution. The unexpected observation is that both of the RLS intensity of AgCl and AgNO_3 system hardly changed with the concentration changes of added NaNO_3 (figures are not presented).

3.3. Stability

The formation process of aggregation particles generally includes three steps: nucleation, crystal growth, and aggregation. The size of the particles is one important factor affecting the RLS production and its intensity. To improve the reproducibility of RLS intensity of a suspension system, it is crucial to impede the rapid sedimentation of the particles. However, the AgCl system is very stable in 40 minutes and

TABLE 1: Effect of interfering ions on the Cl^- determination^(a).

ion	[ion]/[Cl^-]	Change in RLS (%)	ion	[ion]/[Cl^-]	Change in RLS (%)
K^+	10000	0.75	CO_3^{2-}	1000	2.01
Ca^{2+}	10000	1.39	PO_4^{3-}	1000	1.79
Mg^{2+}	10000	1.56	Ac^-	1000	0.88
Zn^{2+}	10000	1.02	HPO_4^{2-}	1000	1.09
Fe^{2+}	10000	1.34	H_2PO_4^-	1000	1.67
Al^{3+}	10000	1.19	I^-	1	6.32
SO_4^{2-}	1000	2.34	SO_3^{2-}	1000	1.86

^(a) The cationic ions were added in the form of nitrate, and the anionic ions were added in the form of sodium. The concentration of Cl^- is 8.52 ng mL^{-1} .

TABLE 2: Determination results of the chloride ion in drinks samples ($n = 5$).

Samples	RLS ($\mu\text{g mL}^{-1}$)	RSD (%)	ISE ($\mu\text{g mL}^{-1}$)	RSD (%)
Mineral water				
Nongfu spring	20.35	1.31	21.19	3.46
Laoshan	N.D		N.D	
Nestlé	37.01	2.43	37.95	1.54
Robust	37.38	1.52	38.53	1.23
Watsons	36.91	2.06	36.40	3.22
Masterkong	38.50	1.33	39.08	1.68
Pure water				
Wahaha	N.D		N.D	
Nongfu spring	N.D		N.D	
Green tea	65.79	1.01	67.06	1.87

the average deviation of RLS signal was found to be lower than 3.80% (figure is not presented). Moreover, the addition order of the reagents has little effect on the RLS spectra.

3.4. Tolerance of foreign ions

There exist a number of cations and anions in drinks. To gain an insight into the RLS selectivity of the AgCl for detection of Cl^- in drinks, the interference of some commonly coexistent ions, such as Na^+ , Zn^{2+} , Ca^{2+} , Fe^{2+} , Mg^{2+} , Al^{3+} , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , PO_4^{3-} , K^+ , and I^- , was investigated under the same conditions. The results demonstrated that the CO_3^{2-} and PO_4^{3-} in excess of 1000 folds in concentration relative to Cl^- influenced the RLS of AgCl (s) particles. This may be due to the formation of extended aggregate around AgCl particle cores by the relatively higher negatively-charged ions of CO_3^{2-} and PO_4^{3-} . I^- in the same concentration relative to Cl^- strongly affected the RLS signal. However, chloride is a prominent negatively charged ion of the drinks. The concentration of I^- is lower than that of Cl^- . Other ions hardly interfered with the AgCl system (Table 1). All concentration of other anions is lower than chloride ion. When the concentration of each ion was the same as or somewhat lower than that of Cl^- , no interference was observed (results were not presented herein). Sodium ion (NaNO_3) hardly exerts interference as well as when its concentration reaches to *ca.* 10000 times that of Cl^- . Therefore, the tolerance levels of the interference of these

coexisting ions in the samples were very high and the assays can be performed without removing them.

4. ANALYTICAL APPLICATIONS

4.1. Detection and quantification limits

The detection and quantification limits were calculated as $s_b + 3s$ and $s_b + 10s$, respectively, where s_b is the average RLS signal of ten blank solutions ($16.99 \mu\text{g mL}^{-1}$ of silver nitrate) and s is the standard deviation. When the RLS intensity at 571 nm was selected, the detection and quantification limit were calculated to be 0.71 ng mL^{-1} and 1.42 ng mL^{-1} , respectively, indicating high sensitivity of this method for the determination of Cl^- . The sensitivity of the RLS method is prominently higher than that of turbidimetry (results are not presented).

4.2. Calibration curve and assay of samples

According to the above standard procedure, the calibration curve was obtained by plotting the concentration of Cl^- against the intensity of RLS spectrum at 571 nm under the optimum conditions (Figure 2). The linear regression equation using the least square method was $\Delta I = -26.97 + 27.25C_{\text{Cl}^-}$ (ng mL^{-1}) ($r^2 = 0.9989$) in the range of $1.42\text{--}8.52 \text{ ng mL}^{-1}$ of Cl^- . The proposed method was applied to determine the concentration of Cl^- in drinks and the results were shown in Table 2.

TABLE 3: Recovery test of some samples.

Sample	Cl ⁻ in sample (μg)	added Cl ⁻ (μg)	found (μg)	recovery range (%)
1	39.2	35.5	75.6–76.7	102.53–105.63
2	36.91	35.5	70.3–71.9	94.08–98.58
3	37.38	35.5	71.9–73.8	97.18–102.53
4	38.50	35.5	72.2–75.9	94.92–105.35
5	37.01	35.5	70.5–74.1	94.37–104.51

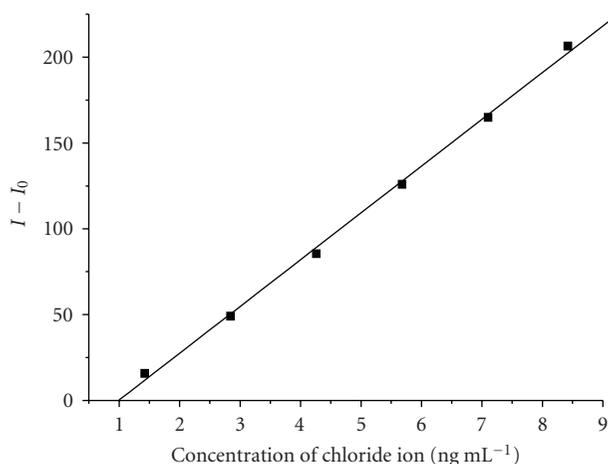


FIGURE 2: The calibration curve of AgCl system at wavelength of 571 nm.

4.3. Recovery

To further examine the accuracy of the proposed RLS method, the recovery experiments were carried out by adding known amounts of Cl⁻ to drinks diluted samples (Table 3). The recovery results were obtained in the range of 94.08–105.63%, which indicated that the proposed RLS method is practical to assay the Cl⁻ in drinks.

4.4. Comparison of RLS and ISE method

The proposed method was applied to determine the concentration of chloride ion in drinks and the results were shown in Table 2. To verify the veracity and practicality, the samples were analyzed simultaneously by the currently used ISE method (Table 2). It can be seen that the results determined by the RLS method were almost in agreement with those by the ISE method. The average RSD of the RLS method is 1.01%–2.43%, which is some lower than that of ISE method (1.23%–3.46%), which proved that the RLS assay in drinks was practical.

These two methods, RLS and ISE, can give the similar results of chloride ion in drinks (Table 2). However, the operations of RLS and ISE methods were significantly different. As we know, ISE method is an electrochemistry analytical method, in which the variation of temperature, fluctuation of voltage, and treatment of electrode may bring on significant influence on the determination though it

features high selectivity. However, the RLS method hardly suffers these factors.

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