

## 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  $\text{Ag}^+$  forming  $\text{AgCl}$  aggregates that produced intense resonance scattering light. Effects of factors such as acidity, ionic strength, and coexistent interferents on the RLS of  $\text{AgCl}$  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  $\text{ng mL}^{-1}$  with a detection limit of 0.71  $\text{ng mL}^{-1}$ . 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  $\text{Cl}^-$  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  $\text{Cl}^-$ . 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  $\text{Cl}^-$  in biological systems. The classical ion-selective electrode method is currently used in food analysis of  $\text{Cl}^-$  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  $\text{Cl}^-$  and to develop an alternative standard method for determination of  $\text{Cl}^-$  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  $\text{Cl}^-$  was prepared by dissolving  $0.5850 \text{ g}$  of  $\text{NaCl}$  (>99.99%, Sigma Co., Mo, USA) in doubly distilled water and diluting to  $1000 \text{ mL}$ . 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.  $\text{HAc}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  ( $0.01 \text{ mol L}^{-1}$ ) were used to control the acidity, while  $0.10 \text{ mol L}^{-1}$   $\text{NaNO}_3$  was used to adjust the ionic strength of the aqueous solutions.

## 2.3. Standard procedure

An appropriate aliquot of  $\text{Cl}^-$  working solution was added to  $1.0 \text{ mL}$  of silver nitrate working solution and diluted to  $10.0 \text{ mL}$  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  $571 \text{ nm}$ . 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  $\text{Cl}^-$ , resp.). The operations were carried out at  $20^\circ\text{C}$ .

## 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  $1.0 \text{ mL}$  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  $\text{Cl}^-$  and  $\text{AgNO}_3$  in water were shown in Figure 1(a) and (b), respectively. It can be seen that the RLS intensity of  $\text{AgNO}_3$  solution is quite weak in the whole scanning wavelength region. In contrast, upon addition of trace amount of  $\text{Cl}^-$  to  $\text{AgNO}_3$  solution, a remarkably enhanced RLS with a maximum peak at  $571 \text{ nm}$  was observed under the same conditions ( $1.0 \text{ mL}$  of silver nitrate). The addition of increasing  $\text{Cl}^-$  to the solution leads to the gradual enhancement in RLS intensity, exhibiting

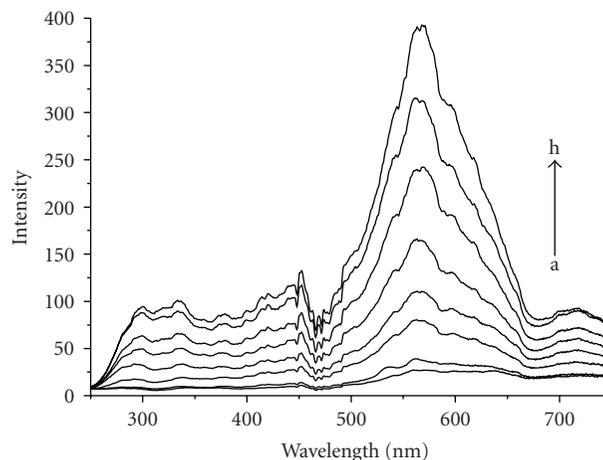


FIGURE 1: RLS profile of AgCl systems. (b)–(h)  $6.99 \mu\text{g mL}^{-1}$  of  $\text{AgNO}_3$ ,  $1.0 \text{ mg mL}^{-1}$  tween-80, and  $0.0, 1.42, 2.84, 4.26, 5.68, 7.10, 8.52 \text{ ng mL}^{-1}$  of  $\text{Cl}^-$ . (a)  $35.5 \text{ ng mL}^{-1}$  of  $\text{Cl}^-$  and  $1.0 \text{ mg mL}^{-1}$  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  $\text{Cl}^-$  ion may displace  $\text{NO}_3^-$  ion in  $\text{AgNO}_3$  (aq), forming a new  $\text{AgCl}$  (s) compound that could be expected to be an aggregate. The size of  $\text{AgCl}$  (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  $\text{AgCl}$  (s) particles may be ascribed to the higher electrostatic attraction between  $\text{Ag}^+$  and  $\text{Cl}^-$  than that of the coexistent  $\text{NO}_3^-$  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  $\text{AgCl}$  and  $\text{AgNO}_3$  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  $\text{AgCl}$  and  $\text{AgNO}_3$  system hardly changed with the concentration changes of added  $\text{NaNO}_3$  (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  $\text{Cl}^-$  determination<sup>(a)</sup>.

ion	[ion]/[ $\text{Cl}^-$ ]	Change in RLS (%)	ion	[ion]/[ $\text{Cl}^-$ ]	Change in RLS (%)
$\text{K}^+$	10000	0.75	$\text{CO}_3^{2-}$	1000	2.01
$\text{Ca}^{2+}$	10000	1.39	$\text{PO}_4^{3-}$	1000	1.79
$\text{Mg}^{2+}$	10000	1.56	$\text{Ac}^-$	1000	0.88
$\text{Zn}^{2+}$	10000	1.02	$\text{HPO}_4^{2-}$	1000	1.09
$\text{Fe}^{2+}$	10000	1.34	$\text{H}_2\text{PO}_4^-$	1000	1.67
$\text{Al}^{3+}$	10000	1.19	$\text{I}^-$	1	6.32
$\text{SO}_4^{2-}$	1000	2.34	$\text{SO}_3^{2-}$	1000	1.86

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

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  $\text{Cl}^-$  in drinks, the interference of some commonly coexistent ions, such as  $\text{Na}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{K}^+$ , and  $\text{I}^-$ , was investigated under the same conditions. The results demonstrated that the  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  in excess of 1000 folds in concentration relative to  $\text{Cl}^-$  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  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ .  $\text{I}^-$  in the same concentration relative to  $\text{Cl}^-$  strongly affected the RLS signal. However, chloride is a prominent negatively charged ion of the drinks. The concentration of  $\text{I}^-$  is lower than that of  $\text{Cl}^-$ . 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  $\text{Cl}^-$ , no interference was observed (results were not presented herein). Sodium ion ( $\text{NaNO}_3$ ) hardly exerts interference as well as when its concentration reaches to *ca.* 10000 times that of  $\text{Cl}^-$ . 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  $0.71 \text{ ng mL}^{-1}$  and  $1.42 \text{ ng mL}^{-1}$ , respectively, indicating high sensitivity of this method for the determination of  $\text{Cl}^-$ . 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  $\text{Cl}^-$  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  $\Delta I = -26.97 + 27.25C_{\text{Cl}^-}$  ( $\text{ng mL}^{-1}$ ) ( $r^2 = 0.9989$ ) in the range of  $1.42\text{--}8.52 \text{ ng mL}^{-1}$  of  $\text{Cl}^-$ . The proposed method was applied to determine the concentration of  $\text{Cl}^-$  in drinks and the results were shown in Table 2.

TABLE 3: Recovery test of some samples.

Sample	Cl <sup>-</sup> in sample ( $\mu\text{g}$ )	added Cl <sup>-</sup> ( $\mu\text{g}$ )	found ( $\mu\text{g}$ )	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

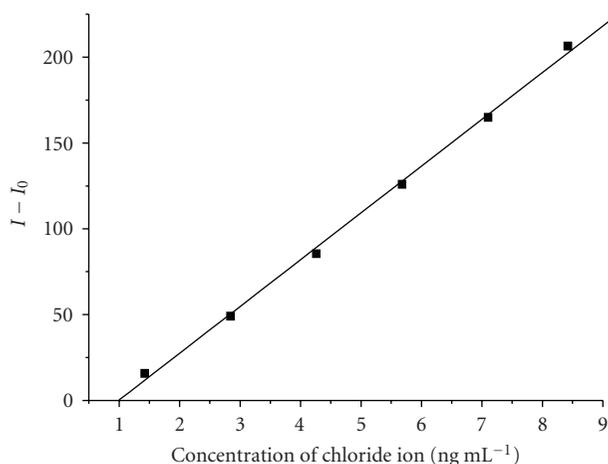


FIGURE 2: The calibration curve of AgCl system at wavelength of 571 nm.

### 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<sup>-</sup> 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<sup>-</sup> 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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