

**SEQUENTIAL ATOMIC ABSORPTION SPECTROPHOTOMETRIC
DETERMINATION OF BINARY MIXTURES OF CHLORIDE -
CARBONATE, CHLORIDE - CHROMATE AND CHLORIDE -
OXALATE IN A FLOW SYSTEM USING AN ON-LINE
PRECONCENTRATION TECHNIQUE**

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Abstract

A method is described for sequential determination of binary mixtures containing each time chloride and another oxoanion (carbonate, chromate and oxalate) using flow injection atomic absorption spectrophotometric method (FI - AAS). The method involves precipitation of the mixture of the two anions with silver nitrate in a Tygon tube containing small glass beads connected to the atomic absorption spectrophotometer, an acid solution is then passed which dissolves the silver oxoanion precipitate in order to determine the oxoanion and then ammonia is passed which dissolves the silver chloride precipitate to determine the chloride. The method allows determination of mixtures with different chloride : oxoanion ratios at the $\mu\text{mol dm}^{-3}$ level, and it is found to be precise, simple and fast.

The analysis of anions is a significant problem in a variety of industries including wine, food and medicine. Numerous methods have been reported both for individual anions or total anionic content. Of particular interest are those using the flow injection analysis (FIA) method^[1] since it allows the possibility of accommodating on-line techniques such as preconcentration which leads to an increase in sensitivity^[2-5]. Many anions have been determined indirectly especially spectrophotometrically^[6-9]. We have reported about the indirect determination of different anions using atomic absorption spectroscopy (AAS). Using this method, the analysis of cyanide^[10], thiocyanate^[10], chloride^[11],

carbonate^[11], bromide^[12], iodide^[12], arsenite^[13], arsenate^[13], dichromate^[14] and oxalate^[14] have been achieved.

Recently interest has increased in simultaneous determination of two or more anions using FIA technique^[15-18]. We have reported the sequential determination of chloride and iodide using FI-AAS technique^[19], depending on the different solubilities of the silver halides in different solvents. Chloride and iodide were precipitated as their silver salts and then ammonia was passed which dissolves the silver chloride but not the silver iodide at that low concentrations, and then cyanide solution is passed which dissolves the silver iodide precipitate. The first obtained signal is proportional to chloride concentration and the second signal is proportional to iodide concentration. Using the same principle we describe in this work the sequential determination of mixtures containing chloride and an oxoanion. Silver oxoanion salts are acid soluble whereas silver chloride is acid insoluble. Therefore in each case after precipitation of the two anions with silver ions acid is passed which dissolves the silver oxoanion precipitate to determine the oxoanion and then ammonia is passed which dissolves silver chloride to determine the chloride concentration.

Experimental

Apparatus :

A Perkin-Elmer 372 atomic absorption spectrophotometer equipped with a silver hollow cathode lamp (4mA) and a strip-chart recorder was used for the FI measurements. The wavelength was adjusted at 328.1 nm, the acetylene and air flow-rates were set to 1 and 8 l.min⁻¹, respectively, and the slit-width was 2 nm. Teflon tubing of 1 mm i.d. from Beckman Altex was used in the flow system. Three Rheodyne loop injection valves (four-ports switching valves) were used to introduce either the washing or the dissolving solution into the precipitating loop. The length of the mixing coil was 5 cm and the i.d. 1 mm. The precipitating loop consisted of a Tygon tube (7 cm x 2.8 mm i.d.) filled with small size Pyrex glass beads (1.9 mm in diameter from Thomas Scientific) was connected

to the switching valve (H) and to the nebulizer of the atomic absorption spectrometer via a Teflon tube (Figure 1). The precipitate was adsorbed on the surface of glass beads. The void volume of the precipitating loop was found to be 85 μl . A (four-channel) peristaltic pump was used to draw the cation and the anion solutions into the precipitating loop and then to waste, and the negative pressure of the nebulizer was used to draw the washing and dissolving solutions through the precipitating loop to the nebulizer of the AAS. The peristaltic pump was connected from one side to the tubes used to draw the silver solution (cation) and the analytes solutions and from the other side to the tubes that bring the solutions to the mixing coil. The flow rate of the dissolving solution was coarsely controlled by adjusting the nebulizer of the spectrometer.

Reagents :

All chemicals were of analytical-reagent grade. Solutions were prepared in distilled-de-ionized water. A standard silver, carbonate, chromate, oxalate and chloride solutions were prepared by dissolving silver nitrate, sodium carbonate, potassium chromate, potassium oxalate and sodium chloride (Merck) which were dried at 120 $^{\circ}\text{C}$ for 48 hours before use. Ammonia 30 % in water, HClO_4 and H_2SO_4 were from Fluka-AG-Chem Fabrik.

Procedure :

Standard solutions of silver nitrate and a mixture of chloride-carbonate or chloride-chromate or chloride-oxalate are passed through the flow system using the peristaltic pump as indicated in the manifold shown in Figure 1. The two solutions mix in the mixing coil and are then pumped to the precipitating loop. Precipitation is allowed to proceed for 2 min under the conditions described in the Apparatus section and then using switching value H the excess of silver nitrate is pumped to waste. The switching valve I first allows a stream of the washing solution (deionized water) to pass to the precipitating loop

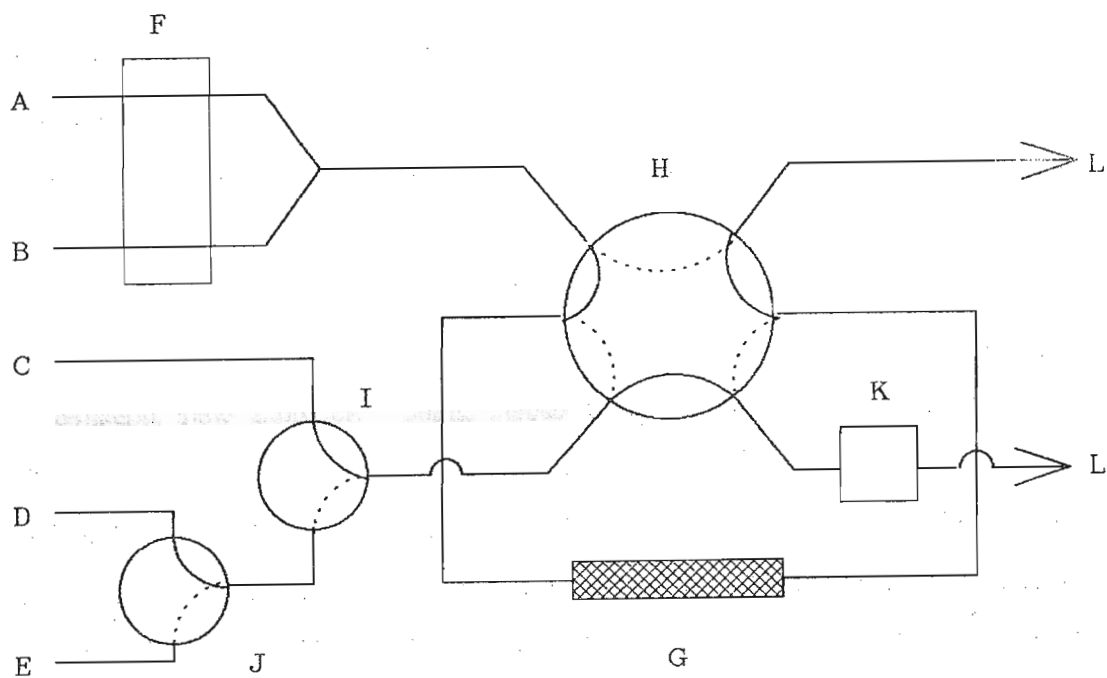


Figure 1 Manifold used for the sequential determination of chloride-oxoanion mixture. A-silver solution ; B-analytes solution ; C-water ; D-acid solution ; E-ammonia solution ; F-peristaltic pump ; G-precipitating loop ; H-J - switching valves ; K-AAS and recorder ; L-wastes .

which all then passes to the AAS until zero response is obtained on the screen. Switching value J allows first a stream of acid to pass which dissolves the silver salt precipitate other than AgCl and carries it all to the nebulizer to be determined and then it allows an ammonia solution to pass to the precipitating loop; this dissolves the AgCl and carries it all to the nebulizer to determine its chloride content. The first AAS signal obtained is proportional to the silver concentration which is in turn proportional to the oxoanion concentration present with chloride in the mixture whereas the second signal obtained is proportional to the chloride ion concentration. During washing of the precipitate, the reading on the screen was followed until it was zero, then the recorder was operated and the responses were recorded during the dissolution process. Time required for washing the precipitate in the presence of chloride is 35, 35 and 33s in case of CO_3^{2-} , CrO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$, respectively. Dissolution of Ag_2CO_3 and AgCl requires 32 and 25s at 1×10^{-4} M of each of CO_3^{2-} and Cl^- . To dissolve Ag_2CrO_4 and AgCl required 31 and 28s at 8×10^{-5} M of each whereas to dissolve $\text{Ag}_2\text{C}_2\text{O}_4$ and AgCl required 35 and 27s at 1.0×10^{-4} M of each.

Results and Discussion

Precipitating the two anions was carried out using a stream of silver ions. The fact that one precipitate is acid soluble and the other is acid insoluble enabled us to determine the concentration of each of the two anions in a mixture. In each determination the different physical and chemical parameters were optimized so as to get the most reproducible and best sensitive results. The results of each pair of anions will be discussed separately. Linear relationships are going to be shown for one system since the others show the same trend. Results of analysis as detection limits and relative standard deviations are shown in Table I.

Table I : Analytical Results of the FI-AAS Sequential Determination of Chloride-Carbonate , Chloride-Chromate and Chloride-Oxalate Mixtures .

| Mixture | Detection Limit ^a (μM) | RSD(%) ^b |
|-----------------------------|---|---------------------|
| a) Cl^- | 2 | 1.2 |
| CO_3^{2-} | 5 | 1.1 |
| b) Cl^- | 2 | 1.2 |
| CrO_4^{2-} | 3 | 1.2 |
| c) Cl^- | 1 | 1.0 |
| $\text{C}_2\text{O}_4^{2-}$ | 6 | 1.1 |

a : Detection limit taken as three times the base line noise .

b : Relative standard deviations at 1×10^{-4} M Cl^- - CO_3^{2-} , 6×10^{-5} M Cl^- - CrO_4^{2-} and 1×10^{-4} M Cl^- - $\text{C}_2\text{O}_4^{2-}$ mixtures for eight replicate measurements .

Chloride-Carbonate Determination

Perchloric acid was used as a dissolving agent for the silver carbonate precipitate and ammonia for dissolution of the silver chloride precipitate. Flow rates of silver ion, the analyte, washing and dissolving solutions were optimized. It was found that the height of the signal increases linearly with increase in flow rate. A flow rate that produces sufficient sensitivity and reasonable reagent consumption was chosen. Flow rates of silver ion solution was 1.4 ml/min, of mixture of Cl^- and CO_3^{2-} was 1.6 ml/min, of washing solution 4.4 ml/min, of HClO_4 solution was 4.2 ml/min and of ammonia solution was 4.0 ml/min.

Effect of silver ion concentration on the response was studied and it was found that the sensitivity increases with increase in the silver ion concentration up to 900 ppm (8 mM) for chloride and 1300 ppm (12 mM) for CO_3^{2-} (Figure 2). To ensure complete precipitation of both anions a concentration of 1300 ppm was used. The effect of concentration of the dissolving solutions (HClO_4 and NH_3) was optimized. For complete dissolution, it was found that 0.08 M HClO_4 and 0.5 M NH_3 are required.

The effect of precipitation time on the response was also studied and it was found that the signal height increases with increase in time up to 16 min at 2×10^{-5} M of both Cl^- and CO_3^{2-} at the optimum conditions (Figure 3). A precipitation time of 2 min was used which produces enough sensitivity and requires reasonable consumption of chemicals. Under the optimum conditions, two calibration graphs were obtained, one for chloride and the other for carbonate (Figure 4). The linear working range is 5-130 and 5-160 $\mu\text{mol.dm}^{-3}$ for chloride and carbonate, respectively. The upper linear limit is believed to be due to saturation of the precipitation loop. Figure 5 shows signals for chloride and carbonate standards. It is clear that the signals are reproducible. If we consider preconcentration time (2 min), washing (35s) and dissolution (32, 25s for AgCl and Ag_2CO_3 respectively) times, then a sampling rate of $\sim 16 \text{ h}^{-1}$ can be achieved using this method.

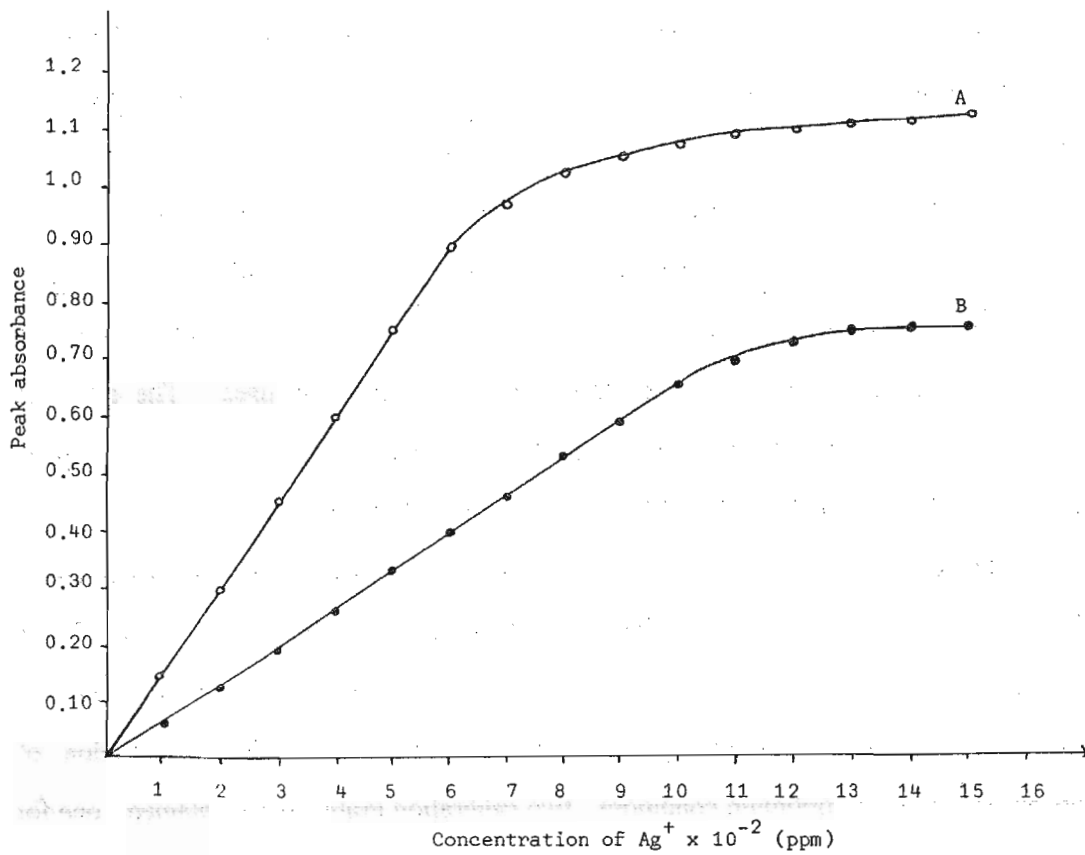


Figure 2 Effect of silver ion concentration on the response of A chloride and B, carbonate.

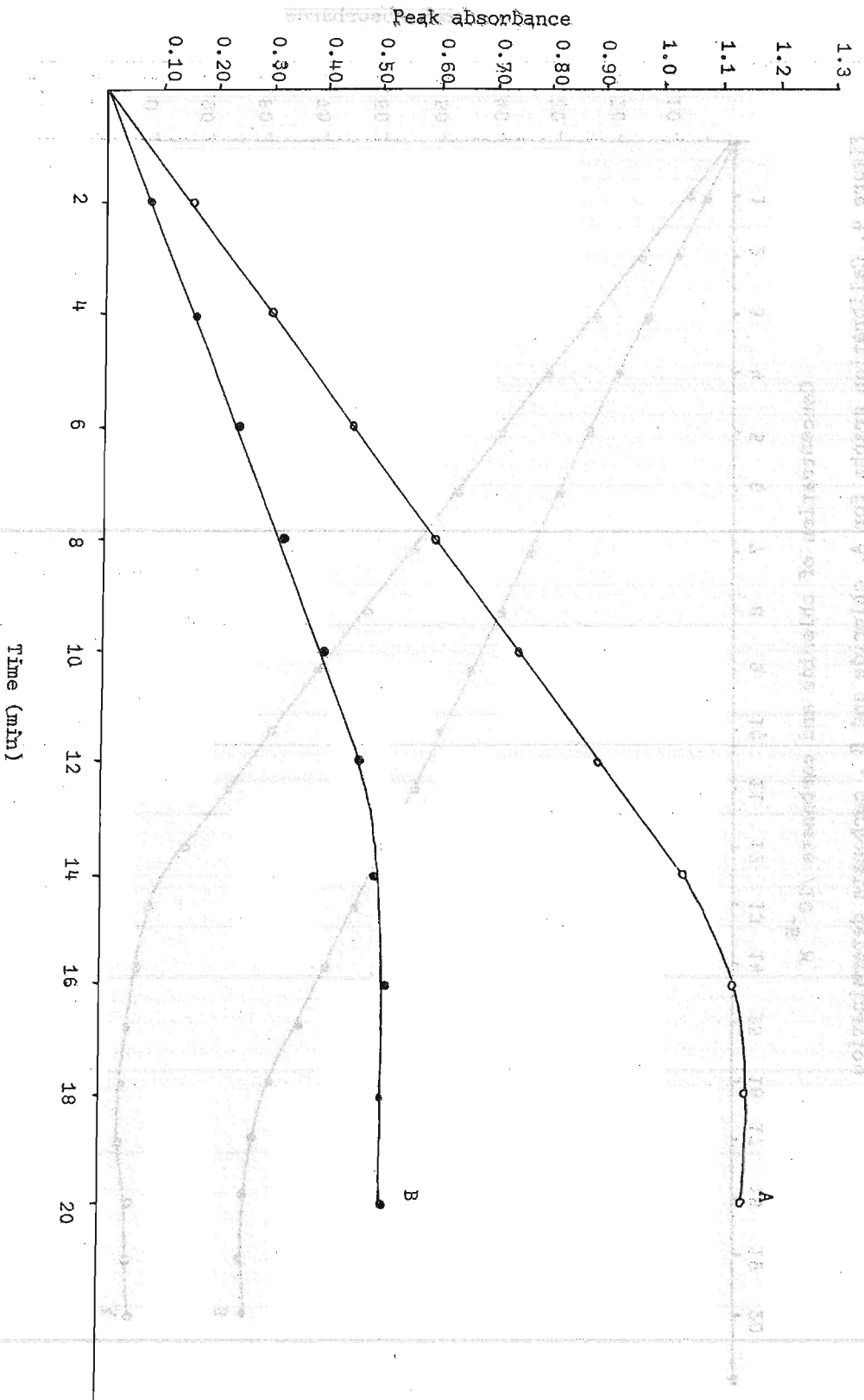


Figure 3 Effect of precipitating time on response of A , chloride and B , carbonate .

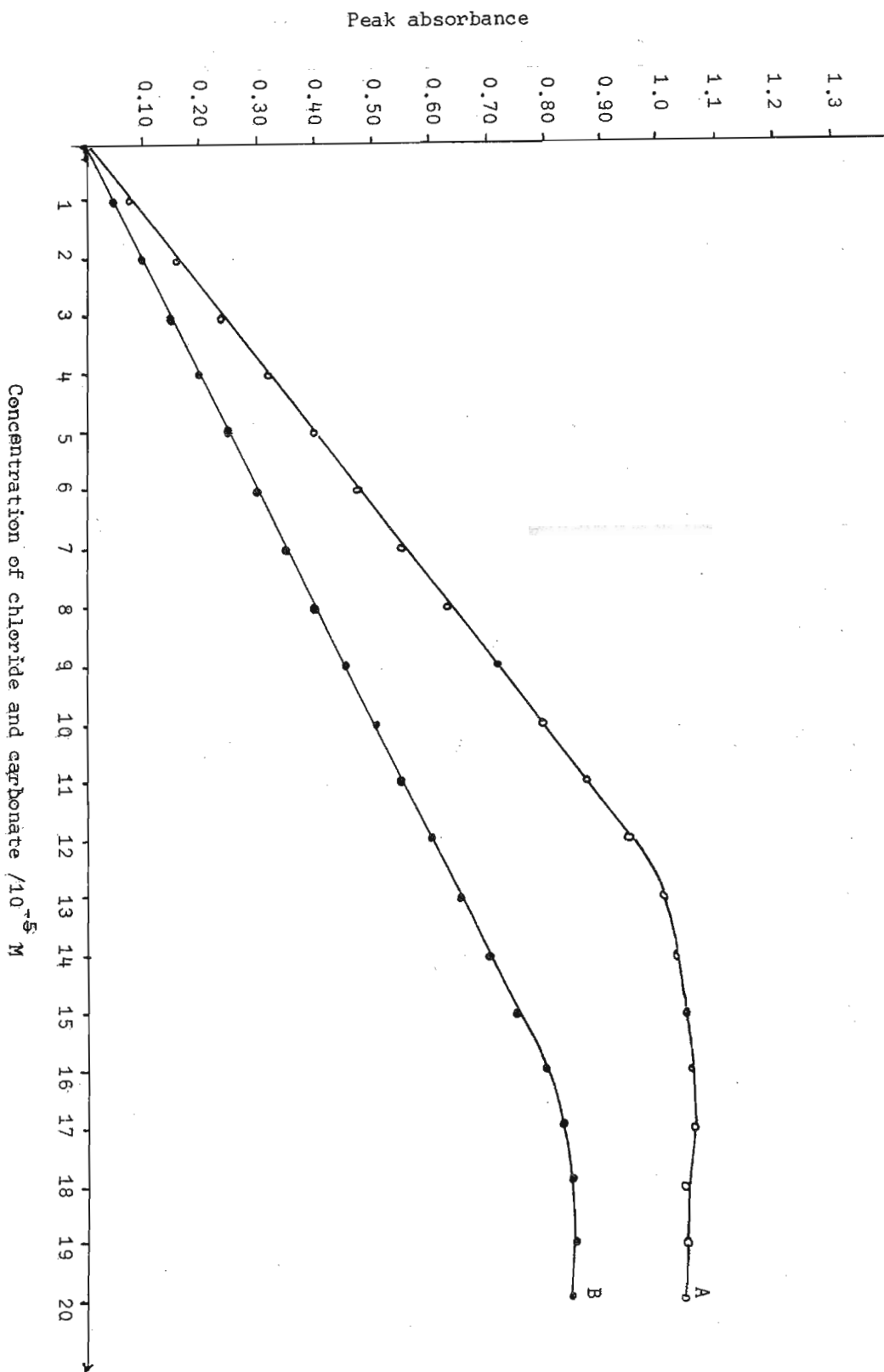


Figure 4. Calibration graphs for A, chloride and B, carbonate determination

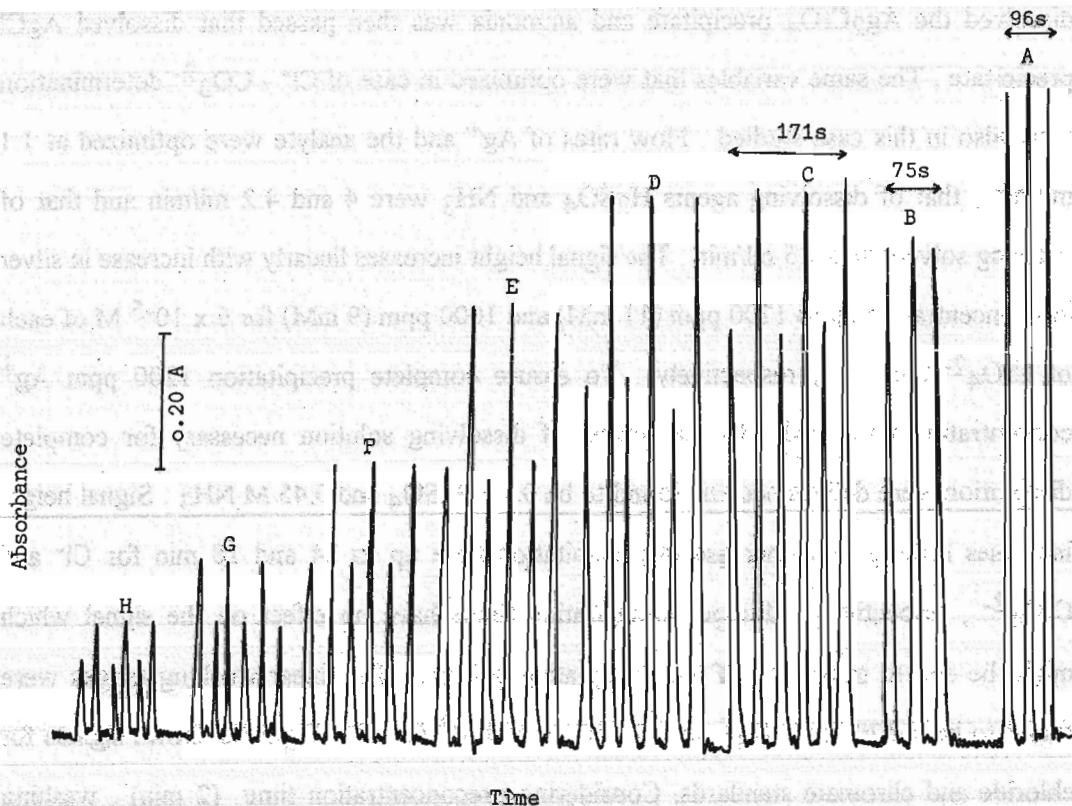


Figure 5 Response of different chloride-carbonate mixtures : A , 1.2×10^{-4} M Cl^- only ; B , 1.4×10^{-4} M CO_3^{2-} only ; C , 1×10^{-4} M Cl^- + 1.2×10^{-4} M CO_3^{2-} ; D , 1×10^{-4} M of each of Cl^- and CO_3^{2-} ; E , 8×10^{-5} M of each of Cl^- and CO_3^{2-} ; F , 5×10^{-5} M of each of Cl^- and CO_3^{2-} ; G , 2×10^{-5} M Cl^- + 5×10^{-5} M CO_3^{2-} and H , 2×10^{-5} M of each of Cl^- and CO_3^{2-} (The chloride peak appears to the right of the carbonate peak in all runs) .

Chloride-Chromate Determination :

Both anions were precipitated by silver ion solution then H_2SO_4 was passed which dissolved the Ag_2CrO_4 precipitate and ammonia was then passed that dissolved AgCl precipitate. The same variables that were optimized in case of $\text{Cl}^- - \text{CO}_3^{2-}$ determination were also in this case studied. Flow rates of Ag^+ and the analyte were optimized at 1.1 ml/min, that of dissolving agents H_2SO_4 and NH_3 were 4 and 4.2 ml/min and that of washing solvent was 4.5 ml/min. The signal height increases linearly with increase in silver ion concentration up to 1200 ppm (11 mM) and 1000 ppm (9 mM) for 6×10^{-5} M of each of CrO_4^{2-} and Cl^- , respectively. To ensure complete precipitation 1200 ppm Ag^+ concentration was used. Concentration of dissolving solution necessary for complete dissolution were determined and found to be 0.10 H_2SO_4 and 0.45 M NH_3 . Signal height increases linearly with increase in precipitation time up to 24 and 18 min for Cl^- and CrO_4^{2-} , respectively. Longer precipitation times have no effect on the signal which might be due to saturation of the precipitating column. The linear working ranges were found to be 5-120 for CrO_4^{2-} and 5-110 $\mu\text{mol}\cdot\text{dm}^{-3}$ for Cl^- . Figure 6 shows signals for chloride and chromate standards. Considering preconcentration time (2 min), washing (35s) and dissolution (31, 28s at 8×10^{-5} M of CrO_4^{2-} and Cl^- , respectively) times, a sampling frequency of $\sim 16 \text{ h}^{-1}$ can be achieved using this method.

Chloride-Oxalate Determination

Precipitation of both anions as their silver salts was carried out and then dissolution of silver oxalate was allowed using HClO_4 followed by dissolution of AgCl by ammonia. For safety reasons one should be cautious not to mix perchloric acid and ammonia solutions. Optimization of flow rates and concentration of chemicals was done and as in case of the former two mixtures the used values were chosen so as to produce reproducible results, sufficient and reasonable reagents consumption.

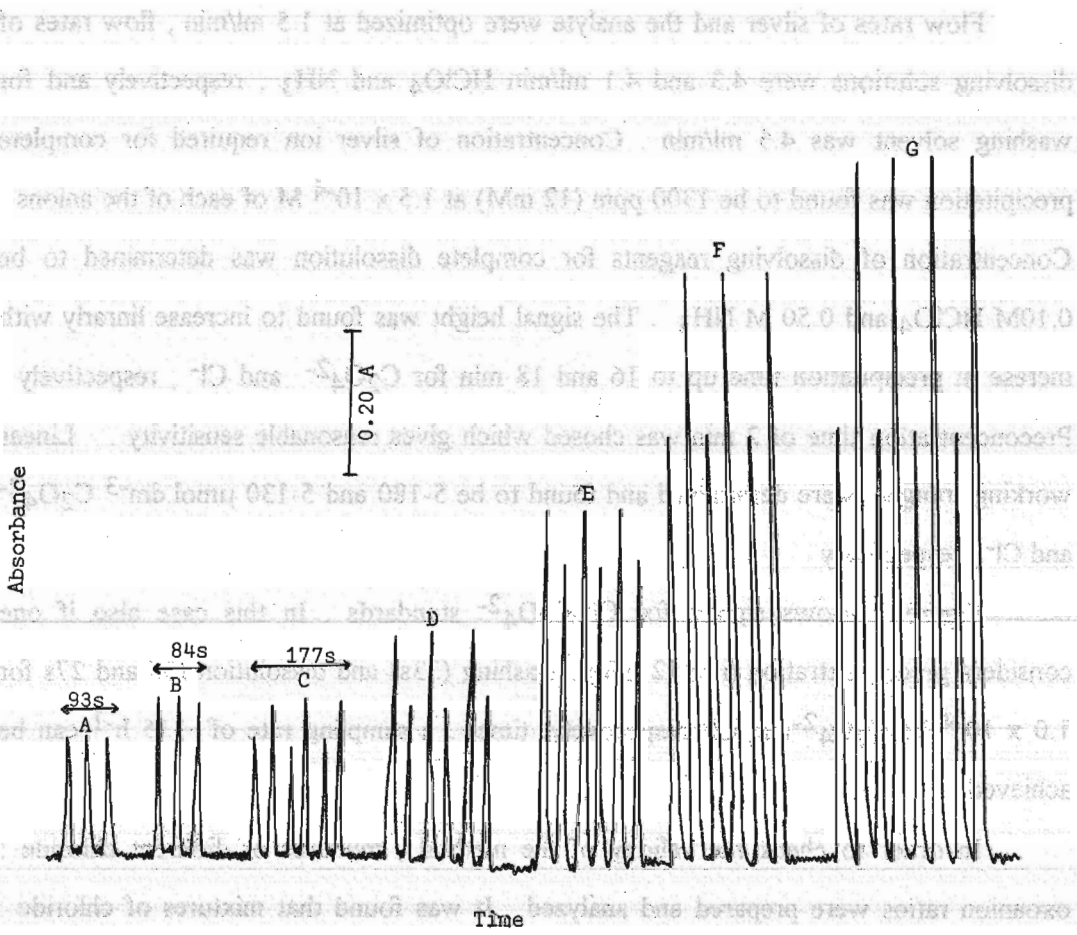


Figure 6 Response of different chloride-chromate mixtures :
 A , 2×10^{-5} M CrO_4^{2-} only ; B , 2×10^{-5} M Cl^- only ; C , 2×10^{-5} M of each of Cl^- and CrO_4^{2-} ; D , 2×10^{-5} M Cl^- + 4×10^{-5} M CrO_4^{2-} ; E , 4×10^{-5} M Cl^- + 6×10^{-5} M CrO_4^{2-} ; F , 8×10^{-5} M of each of Cl^- and CrO_4^{2-} and G , 1×10^{-4} M Cl^- + 8×10^{-5} M CrO_4^{2-} (the chloride peak appears to the right of the chromate peak in all runs) .

Effect of Interference

The interference from foreign ions in the system was studied. The response produced by a solution containing 5.0×10^{-5} M of each anion in each mixture was compared with that containing in addition 5.0×10^{-4} M of foreign ion. The effect of some ions on the analysis is shown in Table III. This table indicates that some ions have a small influence on the response but other especially those that form precipitates with silver ion

Flow rates of silver and the analyte were optimized at 1.5 ml/min , flow rates of dissolving solutions were 4.3 and 4.1 ml/min HClO₄ and NH₃ , respectively and for washing solvent was 4.5 ml/min . Concentration of silver ion required for complete precipitation was found to be 1300 ppm (12 mM) at 1.5×10^{-4} M of each of the anions . Concentration of dissolving reagents for complete dissolution was determined to be 0.10M HClO₄ and 0.50 M NH₃ . The signal height was found to increase linearly with increase in precipitation time up to 16 and 18 min for C₂O₄²⁻ and Cl⁻ , respectively . Preconcentration time of 2 min was chosen which gives reasonable sensitivity . Linear working ranges were determined and found to be 5-180 and 5-130 $\mu\text{mol}\cdot\text{dm}^{-3}$ C₂O₄²⁻ and Cl⁻ , respectively .

Figure 7 shows signals for Cl⁻-C₂O₄²⁻ standards . In this case also if one considers preconcentration time (2 min) , washing (33s) and dissolution (35 and 27s for 1.0×10^{-4} M C₂O₄²⁻ and Cl⁻ respectively) times , a sampling rate of $\sim 15 \text{ h}^{-1}$ can be achieved.

In order to check the validity of the method , mixtures of different chloride : oxoanion ratios were prepared and analyzed . It was found that mixtures of chloride : carbonate ratios ranging from 2:160 to 130:5 $\mu\text{mol}\cdot\text{dm}^{-3}$ can be analyzed . Mixtures of chloride : chromate ratios ranging from 3:140 to 130:3 and mixtures of chloride : oxalate ratios ranging from 1:170 to 140:6 $\mu\text{mol}\cdot\text{dm}^{-3}$ can be analyzed . Table II shows the results of analysis of solutions containing different ratios of Cl⁻ and CO₃²⁻ solution .

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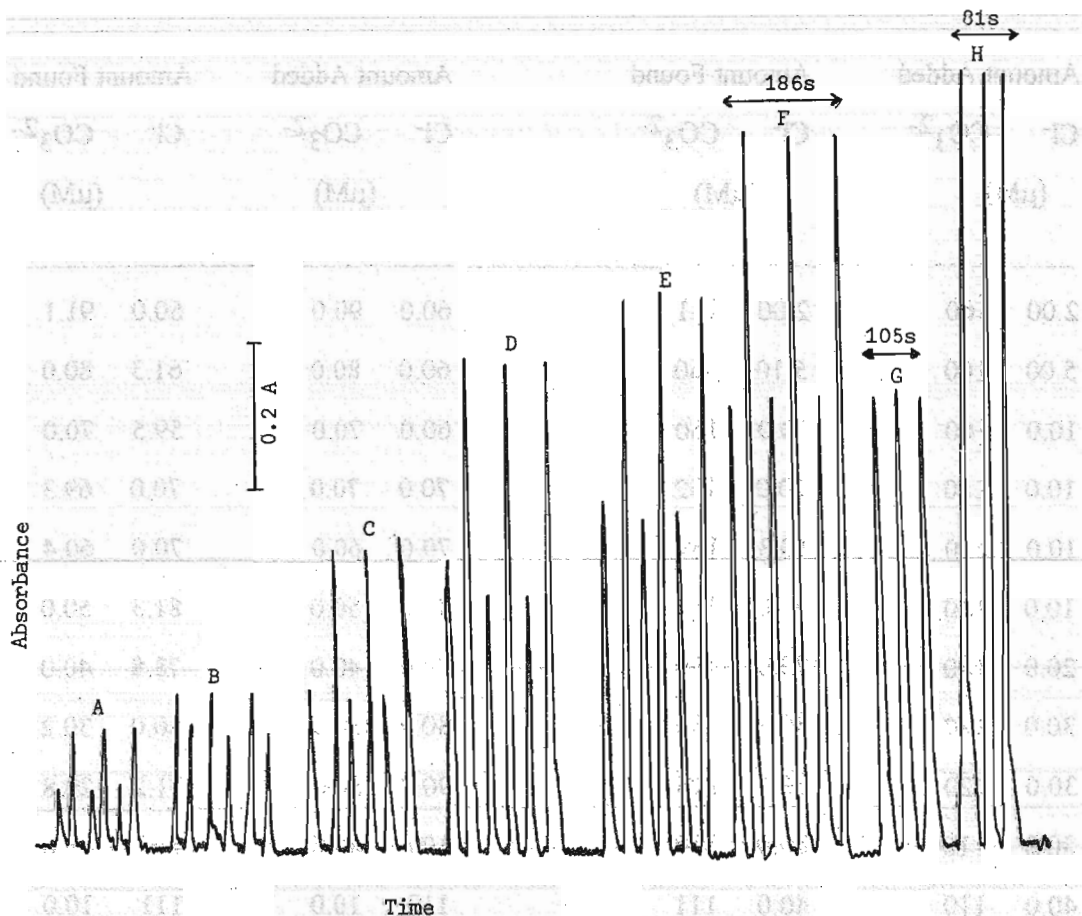


Figure 7 Response of different chloride-oxalate mixtures : A , 2×10^{-5} M of each of Cl^- and $\text{C}_2\text{O}_4^{2-}$; B , 2×10^{-5} M Cl^- + 5×10^{-5} M $\text{C}_2\text{O}_4^{2-}$; C , 5×10^{-5} M of each of Cl^- and $\text{C}_2\text{O}_4^{2-}$, D , 8×10^{-5} M of each of Cl^- and $\text{C}_2\text{O}_4^{2-}$; E , 1×10^{-4} M of each of Cl^- and $\text{C}_2\text{O}_4^{2-}$; F , 1.2×10^{-4} M Cl^- + 1.4×10^{-4} M $\text{C}_2\text{O}_4^{2-}$; G , 1.4×10^{-4} M $\text{C}_2\text{O}_4^{2-}$ only and H , 1.3×10^{-4} M Cl^- only (chloride peak appears to the right of the oxalate peak in all runs) .

Table II: Analysis of Different Chloride-Carbonate Mixtures

| Amount Added | | Amount Found | | Amount Added | | Amount Found | |
|-------------------|-------------------------------|-------------------|-------------------------------|-------------------|-------------------------------|-------------------|-------------------------------|
| Cl ⁻ | CO ₃ ²⁻ | Cl ⁻ | CO ₃ ²⁻ | Cl ⁻ | CO ₃ ²⁻ | Cl ⁻ | CO ₃ ²⁻ |
| (μM) | (μM) | (μM) | (μM) | (μM) | (μM) | (μM) | (μM) |
| 2.00 | 160 | 2.00 | 161 | 60.0 | 90.0 | 60.0 | 91.1 |
| 5.00 | 160 | 5.10 | 160 | 60.0 | 80.0 | 61.3 | 80.0 |
| 10.0 | 160 | 10.0 | 160 | 60.0 | 70.0 | 59.5 | 70.0 |
| 10.0 | 150 | 10.0 | 152 | 70.0 | 70.0 | 70.0 | 69.3 |
| 10.0 | 140 | 10.3 | 139 | 70.0 | 60.0 | 70.0 | 60.4 |
| 10.0 | 130 | 9.70 | 131 | 80.0 | 50.0 | 81.3 | 50.0 |
| 20.0 | 130 | 20.0 | 130 | 80.0 | 40.0 | 78.8 | 40.0 |
| 30.0 | 130 | 30.2 | 130 | 80.0 | 30.0 | 80.0 | 30.2 |
| 30.0 | 120 | 29.7 | 118 | 90.0 | 30.0 | 91.2 | 29.8 |
| 30.0 | 110 | 30.0 | 110 | 100 | 20.0 | 100 | 19.6 |
| 40.0 | 110 | 40.0 | 111 | 110 | 10.0 | 111 | 10.0 |
| 50.0 | 110 | 51.0 | 110 | 120 | 5.00 | 121 | 5.00 |
| 50.0 | 100 | 49.6 | 98.6 | 130 | 5.00 | 129 | 5.00 |
| 50.0 | 90.0 | 50.0 | 90.0 | | | | |

Table III: Effect of Foreign Ions on the FIA-AAS Sequential Determination of Chloride-Carbonate, Chloride-Chromate and Chloride-Oxalate Mixtures

| Ion Added | % Recovery ^a | | |
|--|--|---|--|
| | Cl ⁻ -CO ₃ ²⁻ | Cl ⁻ -CrO ₄ ²⁻ | Cl ⁻ -C ₂ O ₄ ²⁻ |
| F ⁻ | 104-97.6 | 98.6-98.3 | 102-98.0 |
| Br ⁻ | 192-107 | 112-96.0 | 200-93.5 |
| I ⁻ | 119-100 | 150-101 | 200-95.2 |
| CN ⁻ | 75.0-110 | 81.3-133 | 86.3-106 |
| SCN ⁻ | 128-108 | 175-125 | 104-110 |
| C ₂ O ₄ ²⁻ | 90.0-134 | 108-111 | ----- |
| ClO ₄ ⁻ | 103-98.9 | 100-100 | 100-97.9 |
| SO ₄ ²⁻ | 99.0-102 | 96.2-100 | 99.3-96.6 |
| Cr ₂ O ₇ ²⁻ | 80.0-110 | 100-114 | 96.8-113 |
| Pb ²⁺ | 93.5-86.4 | 86.7-60.0 | 95.1-70.3 |
| CO ₃ ²⁻ | ----- | 108-111 | 113-167 |
| NO ₂ ⁻ | 98.8-101 | 100-96.6 | 102-105 |

a Analyte concentration is 5×10^{-5} M and foreign ion concentration is 5.0×10^{-4} M. In each column the first number indicates % recovery of Cl⁻ and the other for that of the oxoanion present in addition to Cl⁻ in each mixture.

or dissolves the silver precipitates as CN^- , SCN^- , Br^- , I^- cause a change in the signal even at low concentrations. The effect of such anions on the response of the analyte can be reduced if a chemical reagent is added that can react with them and stop their precipitation with silver during analysis. This needs a separate study which we will conduct in the near future.

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