

PARAQUAT DICHLORIDE AND DIQUAT DIBROMIDE

Semi-Quantitative Determination and Identity Test for Chloride and Bromide Anions in Paraquat Dichloride Technical and Formulation, Diquat Dibromide Technical and Formulation, and Paraquat Dichloride and Diquat Dibromide Formulation Mixtures

OUTLINE OF METHOD

The weight percent content of chloride anion and bromide anion can be estimated in bipyridinium samples by capillary electrophoresis (CE), using an external standard procedure. The key parameters of this method include the use of an Agilent polyvinyl alcohol (PVA) coated capillary column with indirect ultra-violet (UV) detection and calculation of the chloride anion and bromide anion contents with reference to standards.

The identity of chloride anion and bromide anion can be established by using the CE instrument to fortify samples with calibration solutions.

REAGENTS

0.1N Orthophosphoric acid, aqueous diluted from HPLC grade Orthophosphoric acid (ex Fluka)

Sodium chromate, 98% (ex Aldrich)

Water, purified conforming to ASTM type II

Sodium chloride, standard of known purity

Potassium Bromide, standard of known purity

Electrolyte preparation

Prepare a solution containing approximately 20mM sodium chromate at pH 8.0. For example, to prepare 1 litre: Weigh approximately 3.2g of sodium chromate into a 1 litre plastic bottle. Add 1 litre of ASTM Type II water. Sonicate until completely dissolved and mix thoroughly. Adjust the pH of the electrolyte by gradually adding 0.1N Orthophosphoric acid until pH 8.0 is obtained. Filter the solution using a 0.45µm membrane filter. Degas the electrolyte before use.

Calibration solutions – preparation of solutions for injection

For chloride anion determination or identification: Weigh approximately 40 mg Sodium Chloride standard (WCALCl mg) into a glass bottle (60 ml). Add 50 ml ASTM Type II and shake the bottle until all the sodium chloride has dissolved. Call this solution CCl. Transfer approximately 200µl (using e.g. Gilson Microman pipette) of solution CCl to a CE autosampler vial.

For bromide anion determination or identification: Weigh approximately 50 mg Potassium Bromide standard (WCALBr mg) into a glass bottle (60 ml). Add 50 ml ASTM Type II and shake the bottle until all the potassium bromide has dissolved. Call this solution CBr. Transfer approximately 200µl (using e.g. Gilson Microman pipette) of solution CBr to a CE autosampler vial.

These are the solutions to be injected as calibration solutions, if a semi-quantitative analysis is required. In addition, they can be used as fortifying solutions if an identity test is required.

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APPARATUS

The apparatus listed below was that used to establish the method. Consideration must be given to confirmation of the method on other makes of equipment, providing equivalent performance, to ensure that they are suitable.

Capillary Electrophoresis Instrument equipped with a diode array detector (DAD)

Capillary Column 64.5 cm x 50 μ m (effective length 56 cm) fused silica capillary coated with PVA

Data system

PROCEDURE

(a) *Chromatographic conditions* (typical)

Capillary 64.5 cm x 50 μ m (effective length 56 cm) fused silica capillary coated with PVA ex Agilent part no.: G1600-61219. Green interface required for Agilent 3D CE

Capillary Temperature 20°C

Electrolyte Replenishment For quantitative, reproducible results, replenishment of electrolyte vials is recommended prior to each injection. This can be done by filling vials manually or by using the Replenishment capability, if the instrument can do this. For example:

Function	cm	Vial
REPLENISH	1.8	InHomeVial
REPLENISH	1.8	OutHomeVial

Capillary Preconditioning For quantitative, reproducible results, capillary preconditioning is required. An example of the typical entries in the capillary preconditioning table is shown below:

Function	Time	Inlet	Outlet
FLUSH	2.00 min	I : InHomeVial	O : 48: Waste

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Injection Parameters For semi-quantitative analyses use the following:

Vial	Pressure (mbar)	Time (s)
Calibration/Sample	20	15
I : InHomeVial	20	10

Where identification of an anion is required use the following:

Vial	Pressure (mbar)	Time (s)
Sample	20	15
Calibration (chloride or bromide anion)	20	10

Electrical Parameters

Negative Polarity

Time (min)	Voltage (kV)
0	0
0.2	25

This voltage will generate a current of approximately minus 30-36 μ A

Run Time 5 minutes

Detector Settings

Wavelength	500 nm, Bandwidth 60 nm
Reference	374 nm, Bandwidth 30 nm

Retention times

Bromide anion	approximately 3.4 min
Chloride anion	approximately 3.5 min

(b) Equilibration

Inject portions of the CA or CB solution and check that two consecutive electropherograms are similar to the typical electropherograms shown at the end of the method.

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(c) Preparation of sample

WARNING: *Bipyridinium salts and their solutions are highly poisonous. Bipyridinium salt solutions are corrosive if splashed in the eyes and harmful if allowed to contact the skin or open cuts. Wear eye protection and protective gloves when handling bipyridinium salts, aqueous concentrates and formulated materials.*

Weigh approximately 200-250 mg (200µl) of sample (WS mg) into a bottle (60 ml). Add 50 ml ASTM Type II water and mix well. Call this sample solution S. Transfer approximately 200µl (using e.g. Gilson Microman pipette) of each sample solution S to separate CE autosampler vials.

(d) Determination

Make at least duplicate injections of each calibration and sample in the following sequence:

CCl, S, CCl, S ...for chloride anion analyses and

CBr, S, CBr, S ...for bromide anion analyses

Measure time corrected peak areas in calibration and sample solution injections. The limit of determination for this method is approximately 0.1% w/w for chloride anion and 0.2% w/w for bromide anion in bipyridinium samples.

Confirmation of identity can be established by fortification using the CE instrument. Fortification is achieved by loading a portion of sample solution S onto the capillary followed by a portion of CCl or CBr calibration solution. This can be done by using the appropriate CE instrument injection parameters described earlier in this method. On comparison of an electropherogram resulting from an injection made without fortification with an electropherogram resulting from an injection with fortification, the identity of the anion will be confirmed if the anion peak in question is greater in size for the fortified injection electropherogram and there is an absence of an additional peak.

(e) Calculation

When not calculated by a data system, time corrected peak areas can be calculated as follows:

$$\text{Time corrected peak area} = \frac{\text{Peak area}}{\text{Migration time (s)}}$$

The following calculation is appropriate for the semi-quantitative determination of chloride anion content using the weights and dilutions of standard and samples specified in this method:

For each sample injection solution, the percentage chloride anion content (w/w) is:

$$\% \text{ w/w} = \frac{A' \times P \times 0.607 \times W_{\text{CALCl}} \times 100}{A \times WS \times 100}$$

where:

A' = Time corrected peak area of chloride anion in the sample solution injection

P = Purity of the Sodium Chloride Standard (% w/w)

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0.607 = Factor for the proportion of chloride anion in the standard

WCALCl = Weight taken of Sodium Chloride Standard (mg)

A = Time corrected peak area of chloride anion in the calibration solution injection

WS = Weight taken of sample (mg)

The following calculation is appropriate for the semi-quantitative determination of bromide anion content using the weights and dilutions of standard and samples specified in this method:

For each sample injection solution, the percentage bromide anion content (w/w) is:

$$\% \text{ w/w} = \frac{A' \times P \times 0.671 \times \text{WCALBr} \times 100}{A \times \text{WS} \times 100}$$

where:

A' = Time corrected peak area of bromide anion in the sample solution injection

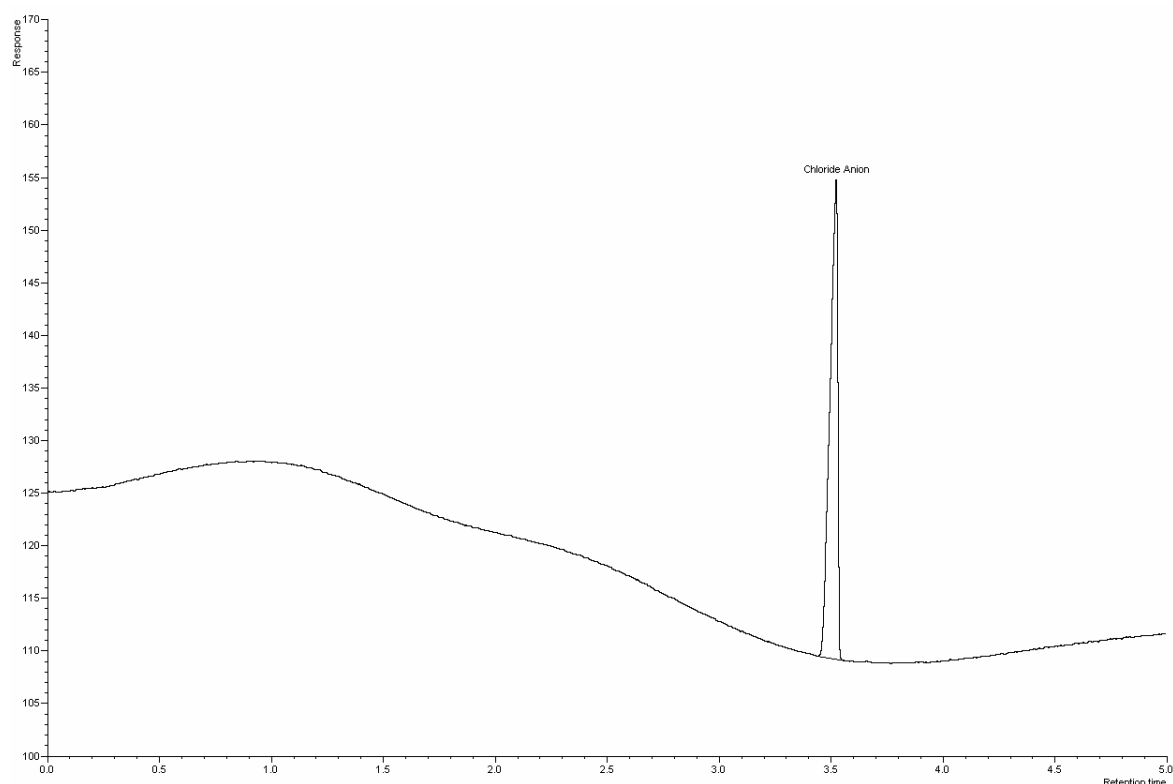
P = Purity of the Potassium Bromide Standard (% w/w)

0.671 = Factor for the proportion of bromide anion in the standard

WCALBr = Weight taken of Potassium Bromide Standard (mg)

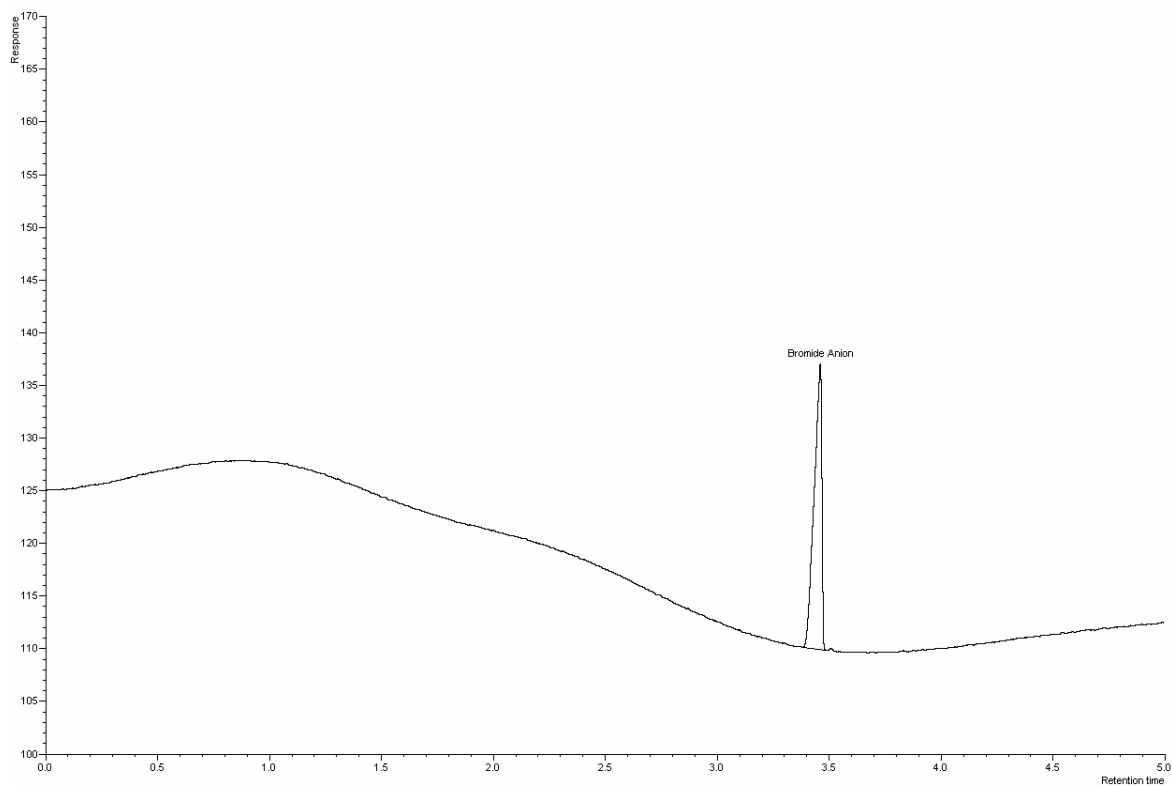
A = Time corrected peak area of bromide anion in the calibration solution injection

WS = Weight taken of sample (mg)

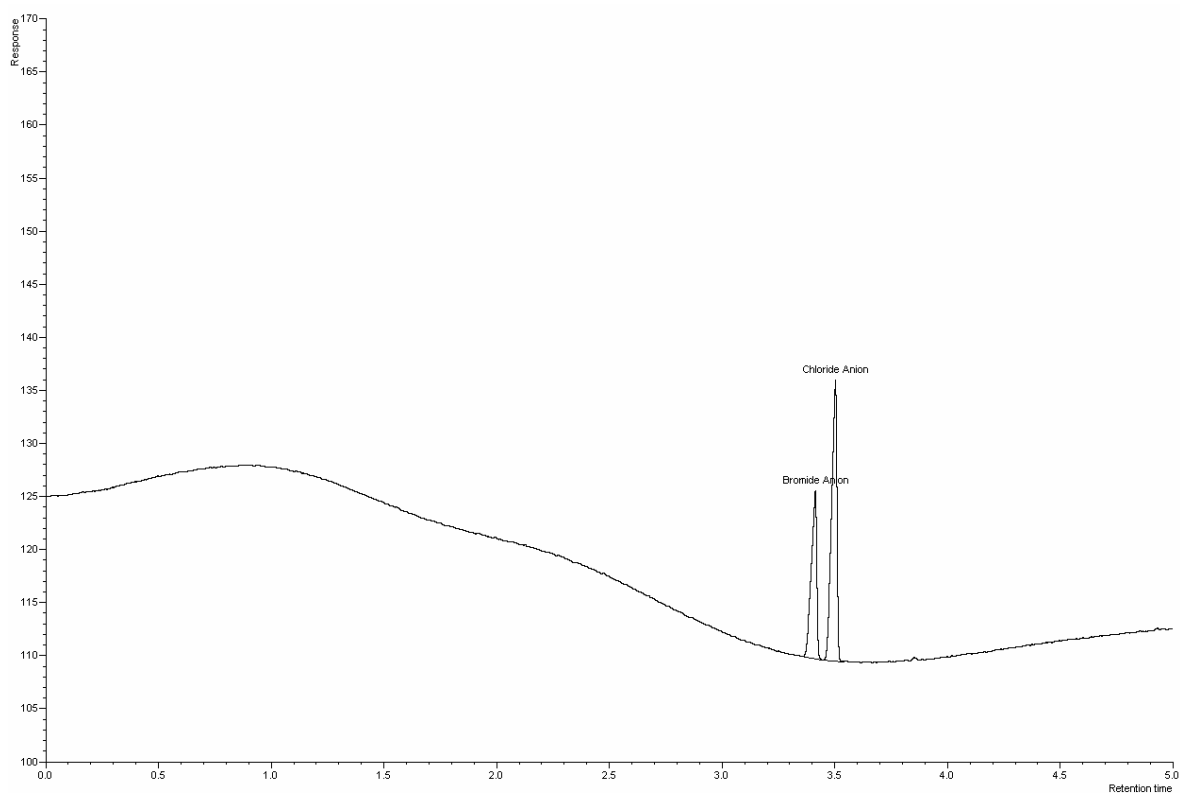


Typical Electropherogram Of Sodium Chloride Calibration Solution

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Typical Electropherogram Of Potassium Bromide Calibration Solution



Typical Electropherogram Of Paraquat Dichloride and Diquat Dibromide Formulation Mixture Solution