

The Research on Analytical Method of Diquat Dibromide in Diquat Technical Concentrates

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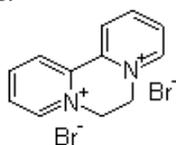
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Abstract. The technical concentrates (TK) is prepared by technical material (TC), the content is lower than TC, it can be used for the preparation of pesticide formulations. Diquat TK is generally brown or dark brown liquid. In recent years, it develops rapidly as herbicides. This paper mainly introduces the research on analyses of the effective components in diquat TK.

1 Introduction

The diquat [1] is light yellow crystal, its ISO name is diquat dibromide, stable in acid and neutral solution, rapidly decomposes in alkaline conditions. Its structural formula is as follows:



2 Experimental Part

2.1 Qualitative analysis

2.1.1 The qualitative analysis of infrared spectrum for diquat TK

The Qualitative Analysis method [2, 3] of infrared spectrum for Diquat TK is as follows:

- Instrument: Spectrum-100 FT-IR Spectrometers.
- Scan range: 4000 cm⁻¹ ~ 400 cm⁻¹.

The diquat dibromide standard samples and diquat TK samples were prepared for the uniform transparent sheet, which will be determined of infrared spectra. The typical infrared spectrum of diquat dibromide is shown in Figure 1.

2.1.2 The qualitative analysis for bromine ion of diquat TK

The reagents and solutions for the qualitative analysis are as follows:

- Water: pure water;
- Potassium bromide standard;

The instruments for the qualitative analysis are as follows:

- Dionex ICS 5000 Ion chromatograph.
- Anion chromatographic column: 250 mm×4.0 mm (i.d.).

The ion chromatography operating conditions are as follows:

- Eluent: KOH solution
- Column temperature: room temperature
- Current velocity (mL/min): 1.2
- Sample volume: 8 L
- Quiescent time: 9.5 min

The determinations of specific steps are as follows:

(1)Preparation of potassium bromide standard solution.

Take an appropriate amount of potassium bromide sample into the volumetric flask, add water to scale, and shake.

(2)Preparation of sample solution

Take an appropriate amount of diquat TK sample into the volumetric flask, add water to scale, and shake.

Under the above mentioned conditions, the retention time of bromine ion in the sample solution of potassium bromide was determined. The typical ion chromatogram for the diquat bromide ion of diquat TK is shown in Figure 2.

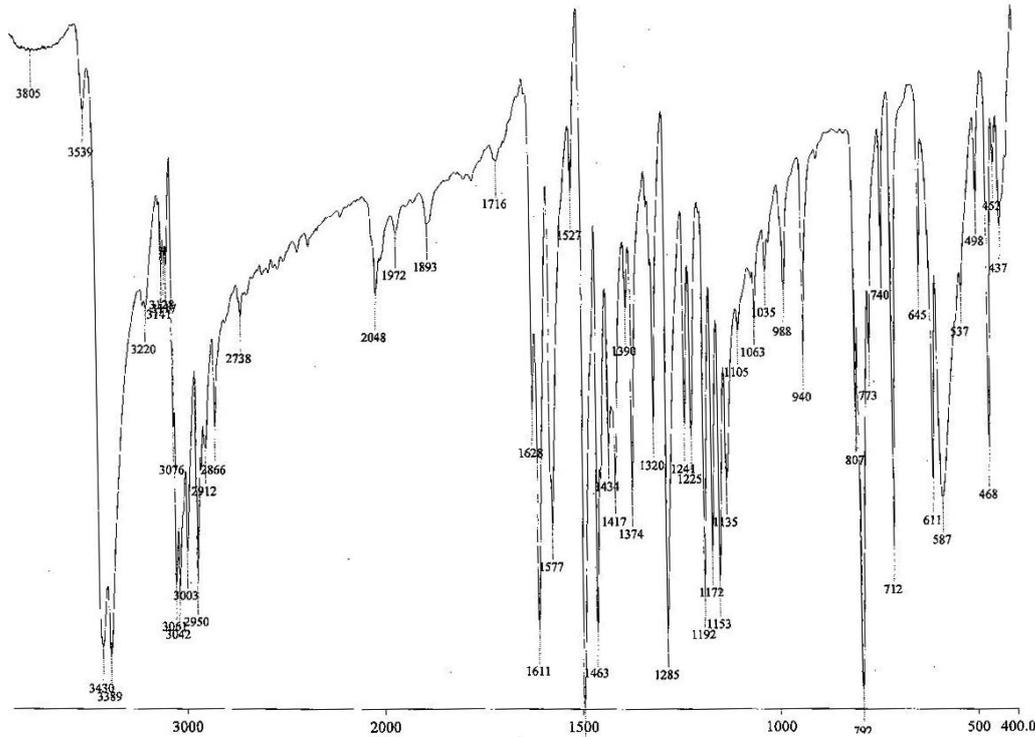


Figure 1. The Infrared Spectrum of Diquat Standard Samples.

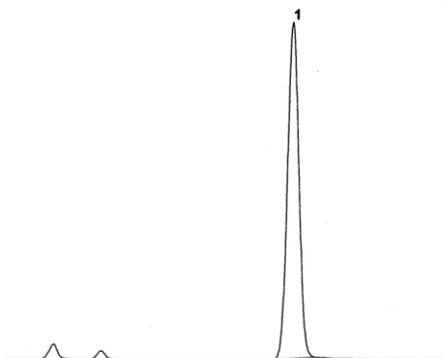


Figure 2. The Ion Chromatogram of Bromine Ion in the Sample.

2.1.3 Liquid chromatography-mass spectrometry

The instrument for Liquid chromatography-mass is as follows [4, 5]:

-Instrument: UPLC Quattro-micro Liquid mass spectrometer.

-Chromatographic column: 150 mm×4.6 mm (i.d.) stainless steel column, filled ZORBAX SB-C18, 5µm filler.

The liquid mass coupling conditions are as follows:

-Mobile phase: ψ (Acetonitrile: 0.1% glacial acetic acid solution) = 5:95.

-Current velocity: 1.0 mL/min.

-Ion source: ESI(+).

-Detection range: m/z 50~1000.

The determinations of specific steps are as follows:

(1) Preparation of standard sample solution

Take an appropriate amount of diquat dibromide samples, which are placed in the volumetric flask, adding acid aqueous solution to the scale, shake.

(2)Preparation of sample solution

Respectively take an appropriate amount of diquat TK samples, which are placed in the volumetric flask, adding acid aqueous solution to the scale, shake.

Mass spectrum determination of diquat dibromide hydrate samples, and the mass spectrum of diquat TK were shown in Figure 3, 4.

From the mass spectrum of diquat TK shown in Figure 3 and Figure 4, we can find that classic date is the same. Some special m/z are 84.7, 157.3, 183.2.

2.1.4 Ultraviolet spectrometry

The instrument for ultraviolet spectrometry [6] is shimadzu UV 2201 ultraviolet spectrophotometer.

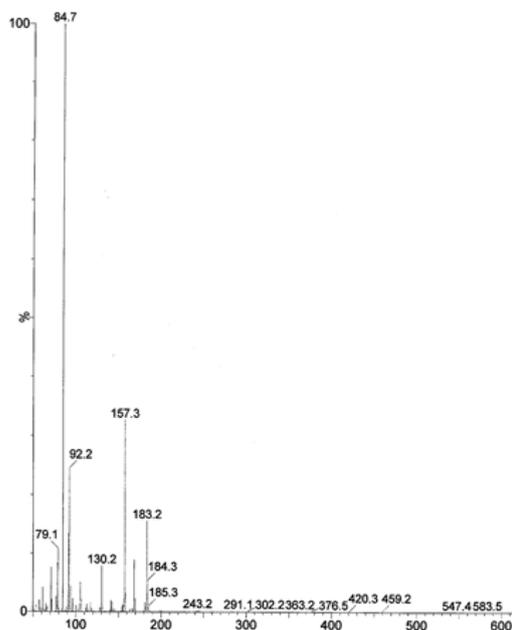


Figure 3. The Mass Spectra of Diquat Samples.

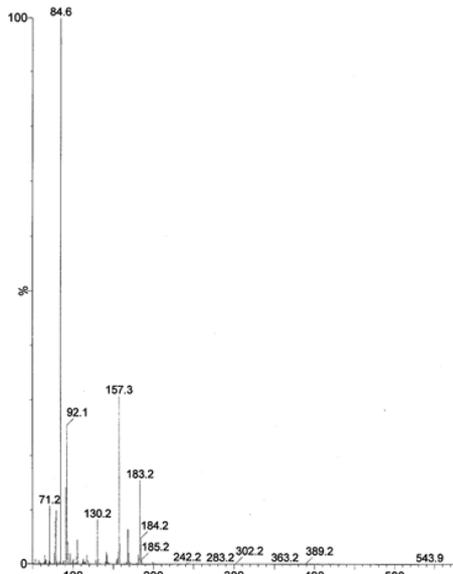


Figure 4. The Mass Spectra of Diquat in Diquat TK.

The ultraviolet spectrum qualitative conditions of diquat standard sample are as follows:

- Light source: deuterium lamp and tungsten lamp.
- Colorimetric pool: 1 cm quartz colorimetric cell.
- Slit: 2.0 nm.
- Scanning range: 400 nm~190 nm.
- Scanning speed: medium.
- Scanning mode: absorbance.
- Solvent: water.
- Reference: water.

Preparation of standard sample solution: take an appropriate amount of diquat standard sample in the sample flask, dissolved with water solution and diluted to the scale, shake, and wait for detection. The typical UV spectra of the diquat standard samples are shown in Figure 5.

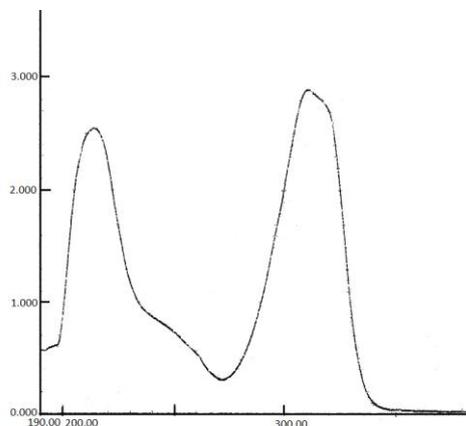


Figure 5. The Ultraviolet Spectra of Diquat Dibromide.

2.2 Quantitative analysis

2.2.1 Reagents and solutions

The specific reagents and solutions [7] are included the following contents:

- Acetonitrile: chromatographic class.

- Phosphoric acid: analytical class.
- Water: ultra pure water.
- Heptanesulfonate: chromatographic pure.
- Triethylamine.
- Phosphoric acid solution: Adjusted with phosphoric acid to pH = 2.1.
- The diquat standard samples.

Heptanesulfonate buffer solution: take an appropriate amount of heptanesulfonate, soluble in 920 mL ultra pure water, adding a certain amount of phosphoric acid, and then mix with triethylamine to a certain pH value, shake.

2.2.2 Method summary

Dissolving the samples in the water, make heptanesulfonate buffer aqueous solution and acetonitrile as mobile phase, stainless steel column and ultraviolet detector with C18 as filler (the maximum absorption wavelength is 310 nm, as shown in Figure 5).

2.2.3 Instrument

- Specific instruments include the following contents:
- HPLC instrument with ultraviolet variable wavelength detector.
- Column: 150 mm * 4.6 mm (i.d.) stainless steel column, filled with C18, 5 m filler.
- Quantitative sampling tube: 5 μ L.

2.2.4 Operating conditions

The HPLC operating conditions [8] include the following contents:

- Mobile phase: heptanesulfonate aqueous solution acetonitrile = 92:8.
- Flow rate: 1.0 mL/min.
- Column temperature: room temperature.
- Wavelength: 310 nm.
- Injection volume: 5 μ L.
- Retention time: the diquat is about 7.8 min.

The high performance liquid chromatography figure of typical diquat TK is shown in Figure 6.

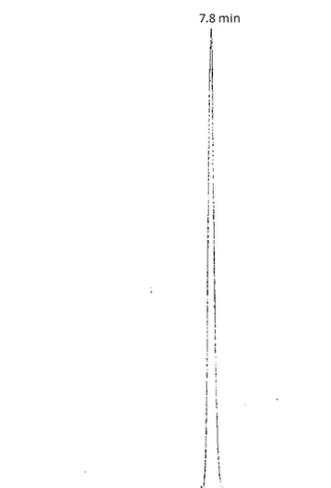


Figure 6. The High Performance Liquid Chromatography Figure of Typical Diquat TK.

2.2.5 Determination

The determinations of specific steps are as follows:

(1) Preparation of standard sample solution

Take an appropriate amount of diquat standard samples into the volumetric flask, add water and shake to be dissolved, dilute with water to the scale, and shake.

(2)Preparation of sample solution

Respectively take an appropriate amount of diquat TK samples into the volumetric flask, add water and shake to be dissolved, dilute with water to the scale, and shake.

2.3 Experimental results and discussion

2.3.1 Linear relationship test

With a certain mass range, the several diquat standard samples were weighed into the different volumetric flasks which have the same volume, dissolved in water, constant volume and shake. According to the operation conditions of the method, the peak area of diquat was determined, and the average results of the two measurements were determined. The standard curve was drew, with the peak area as the horizontal coordinate, the peak area as the vertical coordinateand, the result is shown in Figure 7.

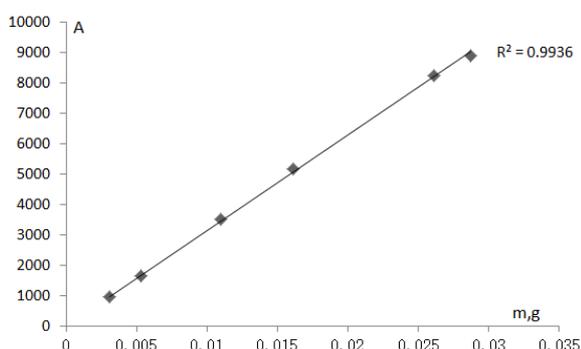


Figure 7. The Relationship Between the Peak Area and Mass Concentration of the Diquat.

From Figure 7, we can see that the diquat dibromide concentration appear a good linear relationship with the corresponding peak area in a certain range, $R^2 = 0.9936$.

2.3.2 Precision test

Select a representative of diquat TK samples (marked 40%), starting from the sample, according to the operation conditions, determination of 6 times, the results are shown in Table 1.

Table 1. The Precision Test results of Diquat TK.

| Measure times | Mass fraction of diquat, % | Range,% | average value,% |
|---------------|----------------------------|---------|-----------------|
| 1 | 40.46 | 0.26 | 40.5 |
| 2 | 40.58 | | |
| 3 | 40.71 | | |
| 4 | 40.55 | | |
| 5 | 40.45 | | |
| 6 | 40.51 | | |

From Table 1, it shows the method has good precision, the determination range is 0.26% with the mass fraction of diquat in diquat TK.

2.3.3 Accuracy test

Take a number of diquat TK together with a certain amount of diquat standard sample. According to the method for the determination of the diquat total quality and the recovery rate was calculated, and the results are shown in Table 2.

Table 2. The Diquat TK Recovery Test Results(%).

| 1# | 2# | 3# | 4# | 5# | 6# | Average |
|-------|--------|--------|-------|-------|-------|---------|
| 99.93 | 100.31 | 101.02 | 99.91 | 99.82 | 99.73 | 100.1 |

3 Conclusion

Firstly, using the infrared chromatography, Liquid Chromatography-Mass Spectrometry, ion chromatography, the determination of bromide ions qualitative methods analysis the diquat TK sample, and then determined by chromatographic methods diquat TK for quantitative analysis.

References

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